

THE DETECTION OF REACTIVE IRON SPECIES AND ASSOCIATED ORGANIC MOLECULES ON MARS AND IN METEORITES

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IMPLICATIONS FOR SAMPLE RETURN

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“There’s just one thing I still don’t understand”

- Gonzo the Great, Muppets from Space

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1. Introduction and Literature Review

Abstract

This PhD project is centred around the preservation potential of organic matter with reactive iron species with application to Mars, meteorites and sample return missions. Mössbauer Spectroscopy will be used to identify these reactive iron species within samples which will be further analysed by different techniques: Raman Spectroscopy, X-ray Fluorescence, X-ray Diffraction, Chemical sequential extractions, and carbon quantification techniques. Mössbauer spectroscopy, X-Ray Diffraction and Raman spectroscopy have already been used by rovers on the surface of Mars'. However, as each rover landed at different places on the surface of Mars, with different analytical instruments, comparative analysis is difficult. This project hopes to start this comparison whilst also investigating general iron mineralogy and redox environments of different samples (Chapter 3).

The identification of iron oxides on Mars is important for preservation of evidence of past life. Both the current Mars 2020 rover, *Perseverance*, and the postponed ExoMars rover, *Rosalind Franklin* are equipped with Raman spectrometers for mineral identification. Identification of iron oxides with Raman spectroscopy can cause dehydration to haematite or fluorescence to overwhelm the resulting spectrum. Within this work, parameters to safely analyse iron oxides with Raman spectroscopy are begun to be investigated and what this means for finding evidence of past life on Mars (Chapter 4).

The techniques listed above will be used on Mars analogues from various sites on Earth to compare mineral detections by the different instruments. Following this, the analogues will undergo sequential extractions to determine the amount of organic carbon bound to reactive iron species within the samples (Chapter 5).

Another aim of this project is to analyse alteration of carbonaceous chondrite meteorites with Mössbauer Spectroscopy and how this relates to the preservation of organic matter (Chapter 6).

Finally, results will be discussed and analysed in the greater context of the importance of mineralogical technique selection and the importance of sample return missions.

Overall, this work aims to highlight the importance of correct mineralogical analytical technique for extraterrestrial missions and why sample return missions are of high importance for understanding geology of bodies other than Earth.

1.1. Habitability of Mars

Habitability of Mars is thought to have changed over time, reflecting the major surface changes Mars has gone through. Mars started out as wet and warm, much like Earth, then major global changes caused Mars to become arid and cold over time, with high UV flux causing the surface to be inhabitable (Bibring et al., 2006; Fairén et al., 2010; Preston and Dartnell, 2014).

1.1.1. Atmospheric Conditions

Early Martian atmosphere was likely similar to the early Earth atmosphere, with a great enough pressure for liquid water to form on the Martian surface (Amils et al., 2007). However, the lower gravity on Mars meant easier escape of hydrogen from the high UV flux of the young Sun (Lammer et al., 2009). Impact-related volatiles and mantle outgassing formed a secondary CO₂ atmosphere (Lammer, 2013), which is 10 times thinner than Earth's atmosphere (Koning et al., 2019). Unlike Earth's atmosphere, the Martian atmosphere does not contain ozone that absorbs harmful UV before hitting the Earth's surface (Cockell, 2000; Cockell and Raven, 2004). To avoid this harmful UV, life is likely to be shielded by ferric iron sediments, halite crystals or snow-ice covers which are known to absorb UV (Amils et al., 2007; Cockell and Raven, 2004).

1.1.2. Surface Habitability Over time

Global mapping of Mars has found three major mineralogical assemblages, representing 3 different climates of Mars (Amils et al., 2007; Bibring et al., 2006; Fairén et al., 2010). These show an early aqueous alteration stage (Phyllocian), an acidic environment (Theiikian) and slow superficial weathering (Siderikian). The Phyllocian is characterised by iron-rich clays like chamosite, nontronite (Bibring et al., 2006; Nixon et al., 2012) and smectite (Fairén et al., 2010). The Theiikian is composed of magnesium, calcium, and iron sulphates (Bibring et al., 2006; Fairén et al., 2010; Preston and Dartnell, 2014; Zolotov and Shock, 2005). Finally, the Siderikian is characterised by iron(III) oxides which lack hydrated minerals (Bibring et al., 2006; Fairén et al., 2010; Preston and Dartnell, 2014; Zolotov and Shock, 2005). Each stage is roughly equated to the major geological eons of Mars (Figure 1.1).

Phyllocian

Thought to be the most habitable era of Mars history (Bibring, et al., 2006; Fairén, et al., 2010). The formation of the clays on Mars is still under debate whether they formed by surface alteration or subsurface alteration (Bibring et al., 2006; Ehlmann et al.,

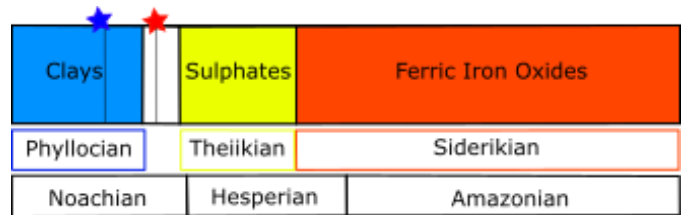


Figure 1.1– schematic timeline of Mars adapted from Bibring et al., (2006). Blue star denotes when the magnetic field vanished, and large impacts stopped (Ehlmann et al., 2012). Red star denotes global volcanism (Bibring et al., 2006; Ehlmann et al., 2012).

2012). Subsurface alteration seems the most feasible formation method as this does not require a dense, warm atmosphere (Bibring et al., 2006; Ehlmann et al., 2012). During this time, the surface was likely wet as evidenced by both the formation of clay (Bibring et al., 2006; Ehlmann et al., 2012) and structures appearing to be ancient lake drainage channels (Fassett and Head, 2008). Towards the end of the Phyllocian, the magnetic field disappeared (Figure 1.1), causing the atmosphere is disappate and become thinner (Ehlmann et al., 2012). This caused the surface to cool down and water to start to freeze (Andrews-Hanna and Lewis, 2011).

Theiikian

The Theiikian started with a global climate change where temperatures lowered (Andrews-Hanna and Lewis, 2011; Fairén et al., 2010) and massive volcanism occurred globally (Figure 1.1) (Bibring et al., 2006; Ehlmann et al., 2012). The sulphates are widespread across Mars, suggesting many sources of sulfur were present on Mars (Bibring et al., 2006). One source of the sulphur is global lava outpourings, emitting volatiles such as water and sulphur into the atmosphere. Water and sulphur would go on to form sulfuric acid which precipitates onto the surface, creating an acidic Mars (Bibring et al., 2006). As volcanism increased, evaporation rates increased, however volatiles like water are lost to space due to solar wind from lack of a magnectic field shielding (Lammer, 2013). As water escaped, the Martian surface got drier over time causing the precipitation of sulphate salts like gypsum and jarosite to deposit (Bibring et al., 2006; Ehlmann et al., 2012; Zolotov and Shock, 2005).

Jarosite

As regional heating occurred, sulphide rich hydrothermal waters deposited pyrite onto the surface of Mars (Zolotov and Shock, 2005). The acidic environment coupled with O_2 in the atmosphere caused oxidation (Bibring et al., 2006) and precipitated goethite and

sulphates like Jarosite (Zolotov and Shock, 2005). Partial neutralisation by silicate dissolution occurred leading to further goethite precipitation, conversion of jarosite to goethite and favoured reaction of Fe(III)-rich concentrations (Zolotov and Shock, 2005). As fluid is consumed, dehydration occurs with regional heating hastening this along, causing the dehydration of goethite to form haematite (Cornell and Schwertmann, 2003; Zolotov and Shock, 2005). At the Meridiani Planum, sulphate-rich layered deposits containing haematite sphaerules were observed by Opportunity (Morris et al., 2019; Nixon et al., 2012), are considered to have formed from the described process above (Zolotov and Shock, 2005). This marks a transition from sulphate deposition to iron oxide deposition.

Siderikian

As Mars got drier, anhydrous iron(III) oxides became the dominating mineralogy (Bibring et al., 2006; Preston and Dartnell, 2014). Atmospheric weathering, peroxide reactivity or frost/rock interactions are responsible for the oxidative conditions on Mars (Bibring et al., 2006). The global distribution of the oxidised iron is due to atmospheric and aeolian transport processes (Bibring et al., 2006; Nixon et al., 2012). The Siderikian is how we currently observe Mars, characterised by hyperaridity, low temperatures and high salinity (Bibring et al., 2006; Fairén et al., 2010; Preston and Dartnell, 2014).

Currently, Mars is unlikely to be habitable due to the dry and oxidative conditions, making finding evidence of past life more likely.

1.2. Fossil Preservation

To find evidence of past life elsewhere, we must study evidence of past life here on Earth. Due to the heavily metamorphosed nature of Earth's early crust (Benton and Harper, 2020; Dodd et al., 2017) finding evidence of the first life on Earth proves to be difficult. The oldest evidence of life discovered so far is dated back to the Early Archean in both the Isua supracrustal belt, Greenland (Dodd et al., 2017; Ohtomo et al., 2014) and the Nuvvuagittuq supracrustal belt, Canada (Dodd et al., 2017). Graphite in the Isua supracrustal belt was found to be depleted in ^{13}C – suggesting biogenic activity (Dodd et al., 2017; Ohtomo et al., 2014). Graphite in the Nuvvuagittuq supracrustal belt was also depleted in ^{13}C whilst having further evidence from hematite and magnetite associations with the carbonate (Dodd et al., 2017).

Fossils are rarely preserved on Earth, often being broken down by surrounding organisms, exposed to oxidising conditions or being physically destroyed (Benton and Harper, 2020;

McMahon et al., 2018). Organic molecules are usually short-lived (McMahon et al., 2018), for example carbohydrates – one of the longest surviving organic molecules – having a half-life of up to 12 Myr (Killops and Killops, 2004). Organic molecules often become nucleation points for minerals, enhancing preservation (Benton and Harper, 2020; McMahon et al., 2018). Iron oxides are known to be minerals that enhance preservation of organic matter (Killops and Killops, 2004; McMahon et al., 2018; Posth et al., 2013, 2014).

1.3. Rusty Carbon Sink

Reactive iron species are capable of bonding with organic carbon, with 21.5 ($\pm$ 8.6%) of all sedimentary organic carbon estimated to be bound to reactive iron (Lalonde et al., 2012). This binding enhances the preservation of organic carbon allowing it to be preserved for longer timescales (Lalonde et al., 2012). The enhanced preservation is thought to be due to strong complexing preventing microbial degradation (Lalonde et al., 2012) the most common cause for organic breakdown on Earth (Killops and Killops, 2004).

Diagenesis also causes to breakdown of organic matter; with labile molecules like carbohydrates and proteins are most susceptible to this (Killops and Killops, 2004). The OC-Fe complexing can prevent this to an extent (Killops and Killops, 2004) causing preservation on timescales of 100,000 years (Lalonde et al., 2012; Posth et al., 2013; 2014).

This stabilisation works also prevents less crystalline forms like ferrihydrite becoming more crystalline over time (Lalonde et al., 2012; Posth et al., 2013; 2014) due to stability against diagenesis (Toner et al., 2012). However, this increased stabilisation might be due to a silicon coating (Toner et al., 2012). It should also be highlighted that in soil, macroaggregates containing iron, form less complexes than finer grained material (Guidi et al., 2021).

On the other hand, artificial maturation studies have shown soluble organic matter is unlikely to be preserved on timescales longer than 100,000 years (Tan et al., 2018, 2021). As discussed below, this can cause issues for finding past life on Mars when Mars was last thought to be habitable during the early Hesperian (Tan et al., 2018, 2021).

1.4. Mars Exploration

Early Mars is thought to have been like the environment on early Earth, meaning it had the potential for life to evolve. Over time, Mars evolved differently to Earth, resulting in the

uninhabitable surface we see today (Preston and Dartnell, 2014; Bibring et al., 2006; Fairén et al., 2010). This is likely due to the loss of the majority of Mars' atmosphere which is linked to the weak gravity causing easier escape of hydrogen gas particles (Lammer et al., 2013). Current missions to Mars have a primary objective to identify evidence of past life (Beaty et al., 2019).

The first successful landing on Mars took place in 1976 with the Viking Landers (Arvidson et al., 1989; Golombek and McSween, 2014). Before this, the Soviet and American space programmes unsuccessfully tried to land a number of missions onto the surface of Mars, along with some successful orbiters and fly-by missions from the American space programme (Golombek and McSween, 2014). Missions to Mars are still popular with different space agencies with several future ones planned.

1.4.1. Viking 1 & Viking 2

Viking 1 landed in the Chryse Planitia and Viking 2 landed on the other side of Mars in the Utopia Planitia along with an orbiter each (Arvidson et al., 1989; Golombek and McSween, 2014). The landers were equipped with scoops and Gas Chromatograph-Mass Spectrometers to try and detect evidence of life (Arvidson et al., 1989). Whilst no organic compounds were detected, potentially due to an oxidising component in the soil (perchlorates as detected by the Mars Phoenix lander and the Mars Science Laboratory rover (Quinn et al., 2013)), a magnetic component of either haematite or maghemite was detected (Arvidson et al., 1989). The Viking orbiters were able to map morphologic units and crater density, allowing geological time periods to be defined: Noachian (>3.6 Ga), Hesperian (3.6-3.0 Ga) and the Amazonian (3.0-0.0 Ga) (Golombek and McSween, 2014).

1.4.2. Mars Pathfinder

The next mission to the Martian surface was the Mars Pathfinder landing on Mars in 1997, carrying the rover *Sojourner* (Golombek, 1997; Golombek and McSween, 2014). Both the lander and rover exceeded their design lifetime to operate for ~3 months with the rover traversing around 100 m around the lander (Golombek and McSween, 2014). The rover was capable of taking photos of the surface at Ares Vallis, showing rounded pebbles of a different composition (as measured by the Alpha Proton X-ray Spectrometer, APXS) to the bedrock suggesting a fluvial origin (Golombek, 1997). The Pathfinder mission did daily Doppler tracking and communicated with the Deep Space Network to observe Mars' moment of inertia suggesting that the planet had a metallic core and was differentiated

(Golombek, 1997; Golombek and McSween, 2014). Overtime, magnetic dust accumulated on the surface of the lander (Golombek, 1997). This was found to contain a small amount of maghemite suggesting iron was dissolved out of crustal material with water again giving evidence for water on the surface of Mars (Golombek, 1997). However, this was further investigated by the Mars Exploration Rovers which discovered that due to the olivine component in the dust, water did not play a role in the formation of the dust (Goetz et al., 2005).

1.4.3. Mars Exploration Rover

The Mars Exploration Rover (MER) mission landed 2 rovers onto the surface of Mars: *Spirit* at Gusev Crater and *Opportunity* at Meridiani Planum in 2004 (Golombek and McSween, 2014; Morris et al., 2019). Both rovers were fitted with Athena science instrument packages which included the Rock Abrasion Tool (RAT), and a Miniaturized Mössbauer Spectrometer (MIMOS II) (best described in Klingelhöfer et al., (2003)). The onboard MIMOS II instrument was capable of detecting ^{57}Fe in different mineral structures with no sample preparation needed (Golombek and McSween, 2014; Morris et al., 2019; Schröder et al., 2016). RAT was used to brush dust away from the surface of the rocks being measured. Whilst only designed to each last 3 months, the rovers exceeded that with *Spirit* lasting just over 6 Earth years and *Opportunity* lasting roughly 15 Earth years (Golombek and McSween, 2014). Whilst both rovers exceeded the mission timeline, readings with the MIMOS II instrument ceased before the mission ended due to ^{57}Co having a half-life of 270 days, meaning integration times for measurements get longer over time until it is no longer viable to conduct measurements (Golombek and McSween, 2014; Morris et al., 2019; Schröder et al., 2016).

Using the MIMOS II instrument, both rovers detected different iron phases at their respective landing sites (Morris et al., 2019; Schröder et al., 2016). Most interesting of these in relation for evidence of ancient life is the presence of nanophase iron oxides (npOx) which can be any of the following minerals: ferrihydrite, hissingierite, schwertmannite, akaganéite, lepidocrocite, superparamagnetic haematite and superparamagnetic goethite (Morris et al., 2019). FeD3 is an unassigned Fe^{3+} phase detected at Meridiani Planum and is also of interest in the search for evidence of past life (Morris et al., 2019). Both are reactive iron species but have slightly differing Mössbauer spectra. As discussed above, reactive iron is able to form complexes with organic matter

prolonging preservation, therefore it can be assumed that the reactive iron detected on Mars could have preserved evidence of past life on Mars.

1.4.4. Mars Science Laboratory

The Mars Science Laboratory (MSL) rover *Curiosity* landed on Mars on in 2012 in Gale Crater (Golombek and McSween, 2014) and is still active presently (Rampe et al., 2020). The rover is equipped with an X-ray Diffractometer (XRD) (Golombek and McSween, 2014; Rampe et al., 2020) which is capable of identifying minerals from crystal structure. Whilst a powerful technique, XRD is unable to identify the composition of clays or the x-ray amorphous component of the soil which can make up to ~40% of the total composition (Rampe et al., 2020). These X-ray amorphous phases have undergone a fitting model and have been assigned to ferrihydrite (Rampe et al., 2020). However, there is no solid evidence for this and could be any of the other phases that fall under the npOx classification.

1.4.5. Mars 2020

Having landed in Jezero Crater in early 2021, the *Perseverance* rover is equipped with a Raman Spectrometer along with several other instruments (Beatty et al., 2019; Bhartia et al., 2021). Jezero Crater is an ancient crater lake with a delta to the northwest which the rover aims to sample as it ascends out of the crater to Nili Planum (Ianson et al., 2021; Stack et al., 2020). Measurements with the Raman instruments, **Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals (SHERLOC)** (Bhartia et al., 2021) and SuperCam (Wiens et al., 2021) are expected to start shortly. The *Perseverance* rover is the first stage of the Mars Sample Return mission which is discussed further in Section 1.5.

1.4.6. ExoMars

ESA's ExoMars rover *Rosalind Franklin* is currently postponed but is planned to land in Oxia Planum on Mars (Quantin-Nataf et al., 2021). The rover will also be equipped with a Raman Spectrometer (Rull et al., 2017) and a drill that can reach depths of up to 2 m to avoid the UV bombarded surface and retrieve unaltered samples (Quantin-Nataf et al., 2021; Vago et al., 2017). Oxia Planum is known to be abundant in Fe,Mg-rich clays as identified from orbit with the High Resolution Imaging Science Experiment (HiRISE) and the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) (Mandon et al., 2021; Quantin-Nataf et al., 2021).

1.5. Mars Sample Return

Mars Sample Return mission is a combination of efforts from NASA and ESA, with the aim of returning samples collected by NASA's Mars 2020 rover *Perseverance* (Beaty et al., 2019; Grady, 2020; Ianson et al., 2021). Samples were expected to return to Earth in the 2030s, however due to current uncertainty in plans this is likely not possible in the current timescale.

1.5.1. Sample Collection

This is a purely NASA endeavour and consists of the Mars 2020 rover *Perseverance*. *Perseverance* is capable of collecting ~35 samples in total which will be split between 2 caches (Ianson et al., 2021).

The first cache will be collected during the prime mission which will last 1 Mars year (~2 Earth years). This cache will be deposited on the rim of Jezero crater after the rover ascends the delta and will contain selected samples from the crater floor and delta (Table 1.1). Duplicates of these samples will remain with the rover and potentially deposited in the second cache. The second cache will also contain samples collected during the potential extended mission if the rover is successful with the prime mission. This extended mission must reach the deposition site of the second cache within 2 Mars years (~4 Earth years) after the end of the prime mission. One of the caches will be selected to collect by the sample retrieval rover, likely the extended mission cache unless the rover dies before deposition of the second cache.

Table 1.1 - Showing samples proposed for collection by the Mars 2020 Rover Perseverance edited from Ianson et al. (2021) with cache 1 being the sample caching after the Prime mission and “keep” meaning the sample will be kept and potentially deposited in the Extended mission

Sample	Suite	Mission	Cache
Delta mudstone	Delta suite	Prime	1
Delta mudstone	Delta suite	Prime	Keep*
Delta curvilinear	Delta suite	Prime	1
Delta curvilinear	Delta suite	Prime	Keep*
Delta-Blocky	Delta suite	Prime	Keep*
Marginal	Marginal deposits suite	Prime	1
Marginal	Marginal deposits suite	Prime	Keep*
Marginal	Marginal deposits suite	Prime	Keep*
Crater rim	-	Prime	1
Crater rim	-	Prime	Keep*
Crater floor	Crater floor rough	Prime	1
Crater floor	Crater floor rough	Prime	Keep*
Crater floor	Crater floor rough	Prime	Keep*
Crater floor olivine-carbonate	-	Prime	1
Crater floor olivine-carbonate	-	Prime	Keep*
Hydrated silica	-	Prime	1

Hydrated silica	-	Prime	Keep*
Blank	-	Prime	1
Blank	-	Prime	Keep*
Ridge-forming fracture	Noachian basement	Extended	*
Olivine-carbonate unit	Noachian basement	Extended	*
Mafic cap unit	Noachian basement	Extended	*
Crater rim layered unit	Rim layered basement	Extended	*
Layered megablock	Rim layered basement	Extended	*
Layered Noachian basement	Megabreccias	Extended	*
Noachian basement	Megabreccias	Extended	*
Crater rim layered unit	Megabreccias	Extended	*
Fracture/vein fill	Megabreccias	Extended	*
Crater rim olivine-carbonate unit	Megabreccias	Extended	*
Megablock	Fractures/vein fills	Extended	*
Fracture/vein fill	Fractures/vein fills	Extended	*
Mafic cap unit	Fractures/vein fills	Extended	*
Layered unit	Fractures/vein fills	Extended	*
Noachian basement unit	Olivine-carbonate-bearing unit	Extended	*
"Blue" megablock	Olivine-carbonate-bearing unit	Extended	*
"Yellow/bright" megablock	Mafic cap	Extended	*
Kaolinite block	Mafic cap	Extended	*
Ridge forming fracture	Layered basin-filling unit	Extended	*

* Sample caching from the Extended mission still undecided

1.5.2. Sample Retrieval

The sample retrieval section of the mission is a combined effort from NASA and ESA set to launch in the future. Originally, NASA was providing the Sample Retrieval Lander which carries the Mars Ascent Vehicle (MAV) and ESA's Fetch Rover and Orbiting Sample canister (OS) (Grady, 2020). The MAV was carrying the OS which in turn will contain the samples collected by Perseverance. This section of the mission was expected to launch in 2026 (Grady, 2020). This section of the mission is currently under review.

1.5.3. Earth Return

Led by ESA, the Earth Return Orbiter was set collect the OS from Mars' orbit and return the samples to Earth as soon as 2031. After this, the samples will then be taken to a Sample Curation facility which is still under discussion on location and number of possible facilities. The Sample Curation facility will be the first stage of planetary protection to ensure no possible Martian life is returned to Earth (Beaty et al., 2019; Grady, 2020). This section of the mission is currently under review.

1.5.4. Knowledge to Gain

Being able to return samples from Mars allows for more analytical techniques to be used rather than just the limited number of instruments on rovers. This also provides the ability to reanalyse samples later with new techniques without the need to send another rover to the surface of Mars. Analysis of the returned samples with Mössbauer spectrometry is important to allow for comparison with the data gathered by the MERs *Spirit* and *Opportunity*. Other reasons include gathering information on reactive iron species, iron mineralogy in general and iron oxidation states to measure alteration.

1.6. Carbonaceous Chondrites and Sample Return

Carbonaceous chondrites originate from organic rich bodies (Pearson et al., 2006) like the asteroids Ryugu and Bennu (Suttle et al., 2021), which have been sampled and returned to Earth recently by JAXA and NASA respectively (Watanabe et al., 2019). Carbonaceous chondrites are a proposed mechanism for delivery of water and organics to an early Earth (Suttle et al., 2021) and record early solar system conditions (Pearson et al., 2006), meaning studying them is important in understanding both the origin of life and solar system formation.

Analysing meteorites with Mössbauer Spectroscopy can be a powerful technique to determine the degree of weathering (Maksimova et al., 2021). Mössbauer Spectroscopy can also be used to identify if a meteorite is classified as a carbonaceous chondrite. This was done with the LAP 03834 meteorite, which was originally classified in the CK3 group of the carbonaceous chondrites but upon analysis with Mössbauer Spectroscopy, it was moved to the R chondrite group due to the lack of magnetite (Maksimova et al., 2021).

Although Mössbauer Spectroscopy is useful for both identifying carbonaceous chondrites and their degree of weathering, only a fraction of carbonaceous chondrites have been

analysed and presented in the literature. Filling this gap could be important to understanding the weathering processes of these meteorites in different environments and will be especially apparent when compared to the fresh material from Ryugu and Bennu along with the relatively fresh material from Winchcombe.

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2. Methods

Below describes the analytical methods and techniques used throughout this thesis. Several methods used reflect instruments on board past, current and future Mars rovers (Mössbauer spectroscopy, XRD, Raman Spectroscopy). Sequential extractions are carried out on Earth analogues to ascertain the amount of organic matter bound to reactive iron species. These sequential extractions underwent microwave digestion, ICP-OES and TC/TN analysis. All methods used are aimed at analysing iron content and how this impacts organic matter within the samples. Sample descriptions are included in the chapter they are analysed in.

2.1. Mössbauer Spectroscopy

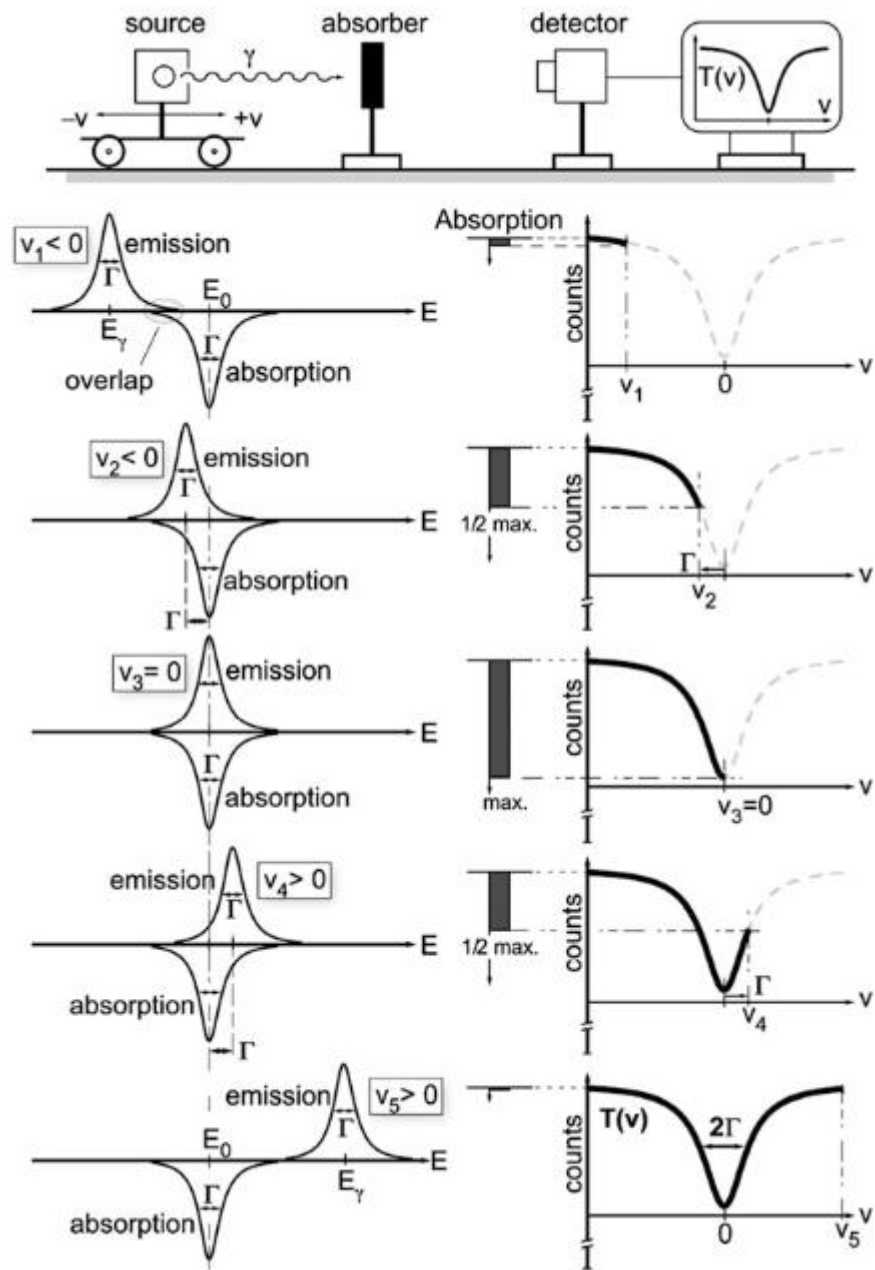
Mössbauer spectroscopy is capable of identifying iron minerals from a small amount of sample in a non-destructive process. Sample preparation can be destructive for low temperature measurements as a powder sample is required. Mössbauer spectroscopy uses a ^{57}Co radioactive source which emit gamma (γ) rays as the ^{57}Co decays into ^{57}Fe . The

γ rays then interact with ^{57}Fe atoms which emit a characteristic photon that is detected and measured to give a spectrum (Figure 2.1). The spectrum can contain sets of peaks called doublets and sextets. Doublets are as the name implies, a set of 2 peaks; similarly, sextets are a set of 6 peaks. Sextets appear when the iron mineral becomes magnetically ordered, the temperature this occurs at is another diagnostic feature of the mineral along with the parameters of the peaks. Transmission and backscatter Mössbauer spectrometers were used in this study. Both instruments used 14.4 keV gamma radiation emitted by a ^{57}Co in rhodium matrix source. The radiation source was in constant acceleration mode (triangular waveform). All spectra were calibrated with an alpha-iron foil (25 μm thickness) spectrum at room temperature.

2.1.1. Transmission Mössbauer Spectroscopy

Transmission Mössbauer spectroscopy is set up so the sample is between the radioactive source and the detector. This results in measurements based on absorption with peaks in the negative. Transmission measurements were carried out at the University of Stirling on a Wissenschaftliche Elektronik transmission Mössbauer spectrometer (Wissel, Germany) with low temperatures achieved with an ICEoxford Dry ICE 4K closed-cycle helium gas cryostat (Figure 2.2). Spectra are evaluated using the Voigt-based fitting routine in the

Recoil software (University of Ottawa, Canada). These measurements are used in



CHAPTERS.

Figure 2.1 - illustration of a Mössbauer transmission experiment in five steps. The "Absorption" bars indicate the strength of recoilless nuclear resonant absorption as determined by the "overlap" of emission and absorption lines when the emission line is shifted by Doppler modulation (figure and caption from Gütlich et al., (2011))

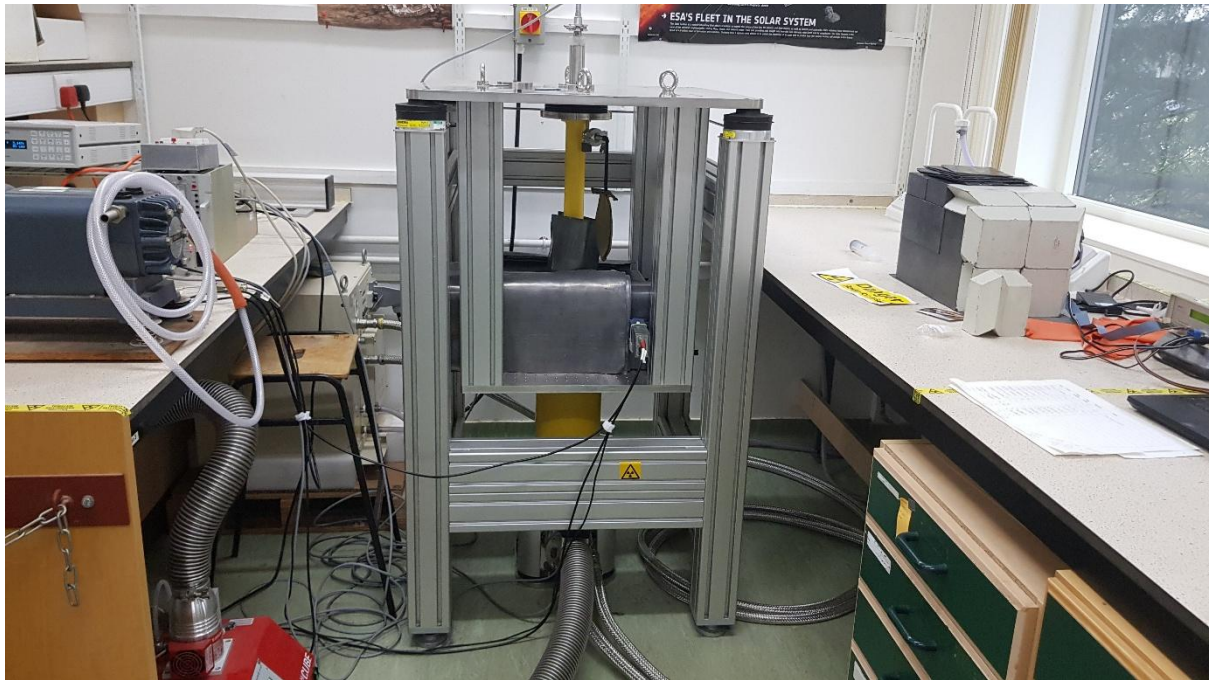


Figure 2.2 - Mossbauer spectrometer set-up at the University of Stirling. Standard Wissenschaftliche Elektronik transmission Mössbauer spectrometer (centre), with the lead castle containing the MIMOS II instrument on the work bench (left)

2.1.2. Backscatter Mössbauer Spectroscopy

Backscatter Mössbauer spectroscopy is set up so the both the detector and radioactive source are on the same side as the sample, with the detector at an angle (Figure 2.3). This results in measurements based on emission with peaks in the positive. Backscatter measurements were carried out at the University of Stirling on a miniaturised Mössbauer spectrometer, MIMOS II (Klingelhöfer et al., 2003). Due to the positive peaks of the spectra, data needs to be manipulated for evaluation in the Recoil software (University of Ottawa, Canada). Data was flipped on the x- and y-axes with a nominal value added to return data into the positive count value, allowing for evaluation of the spectra with the Voigt-based fitting routine in the Recoil



Figure 2.3 - MIMOS II spectrometer at the University of Stirling with a sample placed on top for analysis

software (University of Ottawa, Canada). These measurements are interpreted in **CHAPTER**. MIMOS II instruments were on board the Mars Exploration Rovers, Spirit and Opportunity. Data from the rovers were used in **CHAPTERS**.

2.2. Raman Spectroscopy

Raman spectroscopy is capable of identifying various minerals and organic carbon. No sample preparation is needed and is generally non-destructive (damage can occur during iron oxide analysis, which is discussed further in

CHAPTER). Raman spectroscopy works by a

monochromatic laser of known intensity being focused on a sample (Figure 2.6). The laser interacts with the molecules, with some of the wavelengths being deflected. These deflected waves have characteristic wavelengths depending on the molecules they interact with; this is known as the Raman effect. The deflected waves are detected by a

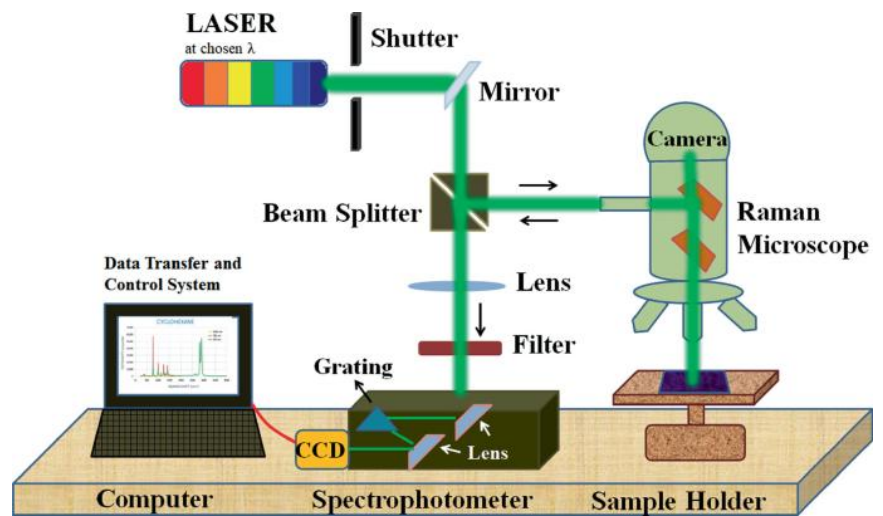


Figure 2.6 - Schematic depicting how Raman spectrometers are set up for sample analysis (From Pandey et al., (2021))

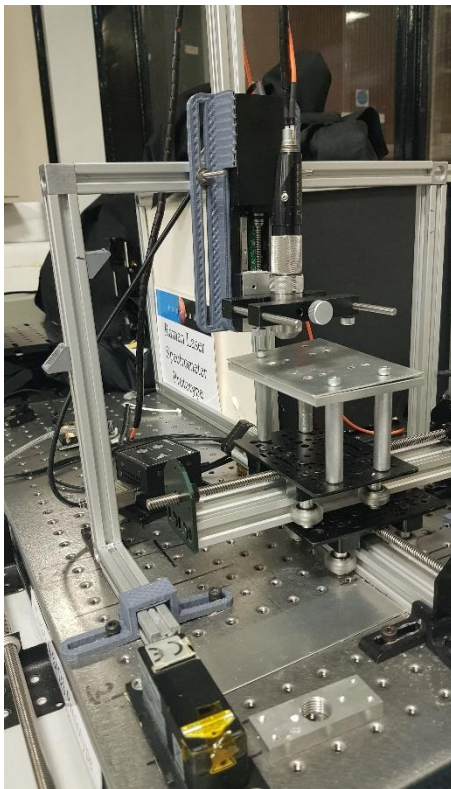


Figure 2.5 - Green laser Raman spectrometer set-up (University of Leicester, UK)

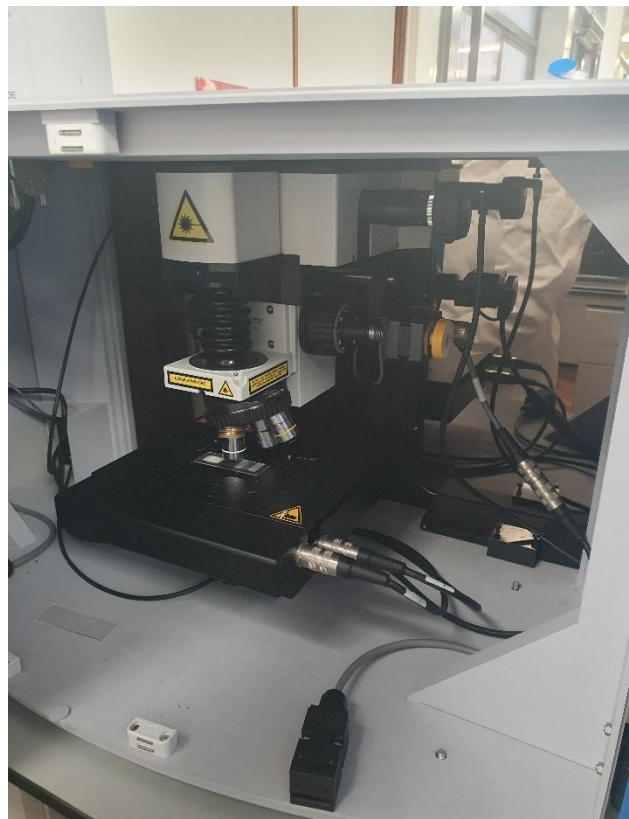


Figure 2.4 - Green laser Raman spectrometer set-up (University of Leicester, UK)

CCD detector. Raman spectroscopy is carried out at the University of Leicester on the ExoMars Raman Laser Spectrometer simulator (Ingley et al, 2011). Laser wavelengths used were 532 (green) (Figure 2.5) and 785 (red) nm (Figure 2.5), with spectra evaluated in Microsoft Excel. Interpretation of Raman spectra is included in **CHAPTERS**

2.3. X-ray Diffraction (XRD)

XRD is a popular technique used in mineral identification. XRD is capable of identifying crystal structure which is diagnostic of the mineral. Sample preparation is destructive as a powder is needed for multiphase analysis; however, the actual analysis is non-destructive. XRD works by an x-ray tube firing x-rays at the sample whilst being rotated around the sample at certain angles (Figure 2.8). The rotation is mirrored by a detector at the same angles. As the angle of the x-ray tube changes, certain wavelengths are deflected differently so the energy of the resulting photon detected by the CCD changes, making this a diagnostic feature. XRD analysis was carried out at the National Museums of Scotland Collection Centre on a Panalytical X'Pert PRO PW3040/60 fitted with a PW3050/60 goniometer in theta-theta configuration (Figure 2.7) with data interpreted in **CHAPTER**. Each sample underwent a 60 second scan, except for sample GC027 B which required a longer scan of 300 seconds. The Mars Science Laboratory rover, Curiosity has an XRD on board. Data from the Curiosity rover's XRD instrument is used in **CHAPTERS**.

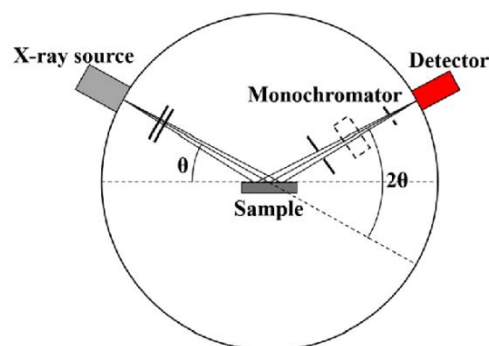


Figure 2.8 - schematic of XRD set-up (From Jung et al., (2023))

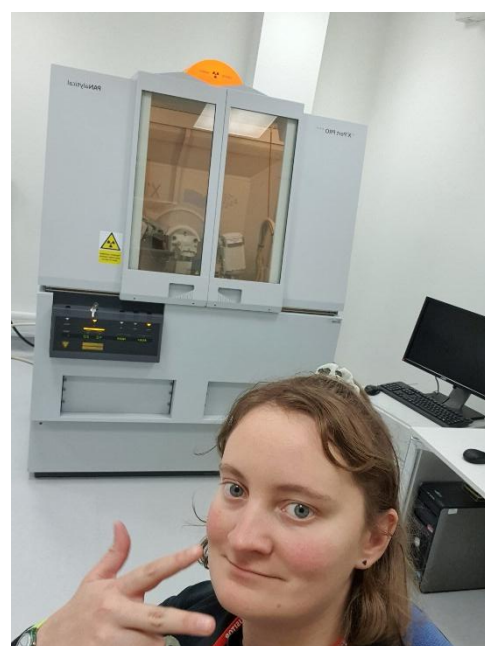


Figure 2.7 - Selfie taken during work using XRD (National Museums Scotland, UK)

2.4. Sequential Extractions

Sequential extractions are a process of dissolving a sample to leave behind components of interest, in this case the amount of organic carbon bound to reactive iron species. The reactive iron species will be dissolved, leaving the organic carbon bound to them behind and allowing for quantification (Lalonde et al., 2012).

1. Every sample was run in triplicate; 2 go through the full dithionite extraction and the third one being the control.

2. ~400mg sample was weighed and transferred into a dry acid cleaned polycarbonate tube.

3. For the dithionite extraction:

- 20.8 ml of 0.11 M sodium bicarbonate and 0.27 M trisodium citrate solution was added to a polycarbonate tube with every sample undergoing the extraction. The polycarbonate tube was then placed in a water bath at 80°C for 15 minutes to heat.

- 0.4 g of sodium dithionite was dissolved in 3.2 ml of the 0.11 M sodium bicarbonate and 0.27 M trisodium citrate solution and added to the pre heated mixture before agitation in the 80°C water bath for a further 15 minutes.

4. For the controls:

- 24 ml of 1.6M NaCl + 0.11M NaHCO₃ solution should be made. 20.8 ml of this was added to the control samples and the polycarbonate tubes then placed in a water bath at 80°C for 15 minutes.

- 0.352 g of NaCl was dissolved in 3.2 ml of the 1.6M NaCl and 0.11M NaHCO₃ solution and added to the pre heated mixture before agitation in the 80°C water bath for a further 15 minutes.

5. Polycarbonate tubes were then removed from the water bath and centrifuged at 6,000 rpm for 10 minutes.

6. Initial supernatant was transferred into acid clean glass vials.

7. Residual sediment in the polycarbonate tube is rinsed with Milli-Q water and centrifuged again. The supernatant is transferred into the same glass vial as before. This set is repeated 3 times.

8. Supernatant is then acidified to a pH less than 2 with concentrated HCl to prevent decomposition.

9. Sediment is then frozen over night at -40°C then freeze-dried, ready for microwave digestion and TC/TN analysis.

2.5. Microwave Digestion

Microwave digestion is carried out on a CEM MARSXpress instrument at the University of Stirling. This is carried out so extracted samples can undergo ICP-OES analysis.

1. ~0.25 g of freeze-dried post-extraction sample was transferred into the bottom of a Teflon microwave tube. In each batch of samples keep at least one tube empty to act as a blank. You should also run a certified reference material (CRM) to check digestion efficiency.
2. 1.5ml (0.75ml) concentrated HCl was added to each tube using a graduated glass pipette, swirling gently and then placing the lid on (not the screw cap), leaving an air gap (the sample should initially react and release gases).
3. Each tube for is left for 15 minutes and then 3.5ml (1.75ml) concentrated HNO₃ was added. Swirled again and left for a further 5 or 10 minutes until frothing has subside. Lid is fully replaced, and screw cap is tightened until hand tight.
4. Tubes are placed in the microwave carousel which was then placed in the digestion unit. The “Soils 3C” programme was run. This program runs for about 50 minutes and then requires about 20 minutes for the cool down program.
5. Once each tube is cooled fully, the contents of the tube were filtered using 150 mm, Whatman No 2 filters. Tubes were rinsed at least 3 times with deionised water. Each sample was diluted to 100 ml with deionised water and stored in acid cleaned plastic bottles.

2.6. ICP-OES

Induced Coupled Plasma Optical Emission spectroscopy (ICP-OES) was carried out on digested samples by Ian Washbourne on a ICAP 6000 series ICP-OES at the University of Stirling. Elements analysed for were Na, K, Ca, Mg, Fe, Mn, Co, Ni, Al, P, Si. This data is interpreted in Chapter 5.

2.7. TC/TN

Total Carbon/Total Nitrogen analysis was carried out on extracted samples by Ian Washbourne on a Elementar EnviroTOC instrument at the University of Stirling. ~10 mg of each sample was weighed and stored in tin capsules prior to analysis. This data is interpreted in Chapter 5.

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3. Reactive iron mineral phases on Mars:

Implications for organic carbon preservation

The following chapter is currently under review with the *Astrobiology Journal*. Figures 3.1, 3.2 and 3.3 have been added here to add further context to measurement geology.

Abstract

It is estimated that ~20% of organic carbon stored in sediments on Earth is bound to reactive iron minerals. They occur often as nanoparticulate or X-ray amorphous iron (hydr)oxides, which are challenging to identify with mineralogical techniques. They are metastable with respect to diagenetic processes. Reactive iron species have been identified on Mars in the form of nanophase ferric oxides in Gusev crater and at Meridiani Planum with Spirit's and Opportunity's Mössbauer spectrometers, respectively, and as Fe-rich amorphous material in Gale crater with Curiosity's CheMin X-ray diffraction channel. Here we use the amount of reactive iron minerals and geochemical evidence for diagenetic processes to assess the preservation potential of sedimentary rocks at these three landing sites. Sedimentary rocks in Gale crater show the highest preservation potential, and organic carbon compounds have been identified in these rocks. Sedimentary rocks in Gusev crater show equally high preservation potential. However, reactive Fe minerals can also react with organic carbon when heat is added during pyrolysis and laser desorption. These effects need to be considered to accurately determine the organic carbon inventory measured during current and future missions as well as in returned samples.

3.1. Introduction

On Earth, it is estimated that more than 20% of all sedimentary organic carbon is bound to reactive iron species (Lalonde et al., 2012). This organic carbon is preserved in oxic marine sediments over million-year timescales (Hepburn et al., 2020; Lalonde et al., 2012). The preservation is mutual because the generally metastable reactive iron mineral phases are also protected from transformation into more thermodynamically stable mineral phases (Schröder et al., 2016). Reactive iron species have a number of definitions (Hepburn et al., 2020; Morris et al., 2006b, 2006a; Raiswell and Canfield, 2012). Here we adopt the description of nanoparticulate Fe(III) (oxyhydr)oxides (npOx) by Morris et al. (2006a, 2006b) as poorly crystalline, solid iron phases, composed of any combination of

lepidocrocite, akaganeite, schwertmannite, iddingsite, ferrihydrite, palagonite or superparamagnetic haematite and goethite. The poorly crystalline and often nanoparticulate nature of reactive iron phases makes them X-ray amorphous, and mineral identification is therefore challenging even on Earth (Hepburn et al., 2020; Von Der Heyden et al., 2019). Proxy methods such as sequential chemical extractions are often used to quantify reactive iron but they are not reliable for mineral identification (Hepburn et al., 2020; Slotznick et al., 2020).

On Mars, reactive iron species have been identified as npOx in sedimentary rocks with the Mössbauer spectrometers (Klingelhöfer et al., 2003) on board the Mars Exploration Rovers (MER), *Spirit* and *Opportunity* (Klingelhöfer et al., 2004; Morris et al., 2004, 2006a, 2006b, 2008, 2019). The Mars Science Laboratory (MSL) *Curiosity* rover does not carry a Mössbauer spectrometer. But with the X-Ray Diffraction (XRD) channel of its Chemistry and Mineralogy (CheMin) instrument (Blake et al., 2012), it identified iron-rich X-ray amorphous material (AmoFe) (Rampe et al., 2017, 2020) whose properties are described in a remarkably similar way to npOx (Table 3.1).

Table 3.1 - Similarities between npOx and AmoFe observed by MER and MSL

	MER Spirit and Opportunity Rovers^a	MSL Curiosity Rover^b
Instrument used:	MIMOS II	CheMin-XRD
Found as:	Nanophase iron oxides (npOx)	Iron rich X-ray amorphous material
Description:	Poorly crystalline or short-range order octahedral Fe ³⁺ . Predominantly (super)paramagnetic iron oxides/oxyhydroxides.	Truly amorphous and short-range atomic order iron and titanium rich material.
Incorporates:	Anions such as SO ₄ ²⁻ , Cl ⁻ and PO ₄ ³⁻	Volatiles such as SO ₃ , Cl, and P ₂ O ₅

^a(Morris et al., 2019) ^b(Rampe et al., 2017)

We posit that both npOx and AmoFe represent reactive iron mineral phases. Because they are present at three spatially distant landing sites that expose rocks deposited around the

Noachian/Hesperian transition, we can infer that reactive iron minerals are widespread in sediments from these epochs. This is corroborated by the recent finding that Mars' red colour may stem from the presence of the poorly crystalline, hydrated iron oxide ferrihydrite in the martian dust (Valantinas et al., 2025). The mineral must have formed when the planet was still wet, and it is stable under current environmental conditions.

The presence of reactive iron minerals in sedimentary rocks indicates their enhanced potential for organic carbon preservation in two ways. Firstly, analogous to Earth, reactive iron minerals might have preserved any organic carbon deposited in the original sediments. Secondly, because reactive iron species are metastable, their presence indicates that these rocks have only undergone mild diagenetic alteration processes. Diagenesis is defined as any process which physically and chemically modifies the originally deposited sediment when it becomes a sedimentary rock, which occurs between deposition and before weathering, erosion, or metamorphism. (Milliken, 1978; Siebach et al., 2014). These processes include fluid movement through the lithified rock as well as the addition of pressure or heat or any combination thereof. Evidence for these processes on Mars has been visually observed in the form of concretions and nodules, dark raised ridges, bleached zones or mineral vugs and veins (e.g. Bristow et al., 2021; McLennan et al., 2005; Morris et al., 2008; Rampe et al., 2020; Siebach et al., 2014). Ion exchange between fluid and the rock removes soluble ions like Fe^{2+} , Ca^{2+} , K^+ and Na^+ and deposits them elsewhere, whilst insoluble ions like Al^{3+} will remain (Bonsall et al., 2023; Hurowitz et al., 2006; Liu et al., 2021). Organic compounds associated with minerals that are dissolved or destabilized in this way lose their protection and may be destroyed (Bristow et al., 2021). Added heat not only results in dehydration and transformation of mineral phases but - in the case of reactive Fe minerals - can also lead to reactions between Fe minerals and associated organic compounds where the latter are oxidized and the Fe is reduced, again leading to the loss of organic compounds (Posth et al., 2013; Schröder et al., 2016; Tan et al., 2021).

While the presence of reactive Fe minerals indicates an enhanced potential for organic carbon compound preservation, they can negatively affect the measurement of these organic compounds. The heat introduced via lasers - e.g. from Raman spectrometers such as Perseverance's Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals (SHERLOC) instrument (Barthia et al., 2021) or the Raman Laser Spectrometer (RLS; Rull et al., 2017) and the Mars Organic Molecule Analyzer's (MOMA; Goesmann et al., 2017) laser desorption mass spectrometer channel for the

Rosalind Franklin rover – dehydrates and transforms reactive iron minerals into haematite (Hanesch 2009; Bonsall et al. 2022; Schröder et al. 2025) and may result in redox reactions with any associated organic compounds. Heat from pyrolysis for Gas Chromatography Mass Spectrometry (GCMS) – e.g. from Curiosity’s Sample Analysis at Mars (SAM) instrument (Mahaffy et al., 2012) or Rosalind Franklin’s MOMA – will act in a similar way. It has been shown that the composition of organic compounds changes when measured via pyrolysis GCMS in the presence of reactive Fe minerals (Royle et al., 2021; Sephton et al., 2023; Tan et al., 2018, 2021).

Here we assess the relative organic carbon preservation potential of sedimentary rocks at three rover landing sites – Gusev crater, Meridiani Planum, and Gale crater – by investigating the presence of reactive Fe minerals versus observed diagenetic features. Because reactive Fe minerals were identified with different instruments - Mössbauer spectrometers (Klingelhöfer et al. 2003) on board the Mars Exploration Rovers Spirit (Gusev crater) and Opportunity (Meridiani Planum) and the X-Ray Diffraction (XRD) channel of the CheMin instrument (Blake et al., 2012) on board Curiosity (Gale crater) - we use data from the Alpha Particle X-ray Spectrometer (APXS; Rieder et al., 2003; Campbell et al. 2012) on board all three rovers to allow for a quantitative comparison. Geochemical data obtained with the APXS also enable us to constrain diagenetic alteration processes that acted on the sedimentary rocks investigated. Because out of the three rovers only Curiosity is equipped with an instrument for organic molecule analysis (SAM), only rocks in Gale crater could be assessed for the actual presence of organic compounds. We then discuss the implications for current and future organic carbon measurements in situ on Mars or in returned samples.

3.2. Materials and Methods

3.2.1. Landing site geology and target selection

Gusev crater: Gusev crater was selected as the landing site for Spirit because the large inflow channel Ma’adim Vallis and delta-like deposits at its mouth are evidence that the crater once held a lake. However, Spirit landed in the central plains which are covered by basaltic lava flows dominated by impact and aeolian features. Adirondack class rocks (Morris et al., 2006a) are part of these lava flows and are used throughout this study as a

reference point, representing largely unaltered basaltic rock. The Columbia Hills are embayed by the lava flows and represent older material from the Noachian/Hesperian boundary (Arvidson et al., 2008; Crumpler et al., 2011). Spirit spent the majority of its mission investigating these hills. The rock types in the Columbia Hills do not represent lake sediments. They are of volcanic origin (Squyres et al., 2006) but many present as clastic, layered rocks that have been altered by aqueous fluids and were therefore included in this study. Of these, Clovis class rocks (Ming et al., 2006; Morris et al. 2006a; Squyres et al. 2006) contain the Fe hydroxide goethite (Klingelhöfer et al., 2005) and possibly phyllosilicates (Morris et al., 2008; Ruff et al., 2006; Wang et al., 2006). Barnhill class rocks (Ming et al., 2008; Morris et al., 2008) make up Home Plate, a roughly circular plateau comprised of layered pyroclastic material (Squyres et al., 2007; Lewis et al., 2008). Barnhill class rocks have experienced high and low temperature aqueous alteration (Schmidt et al., 2008, 2009). Home Plate is surrounded by fumaroles (Wang et al., 2008; Yen et al., 2008) and evidence of an ancient hot spring environment (Ruff et al., 2020; Squyres et al., 2008). In this area, layered Halley and Montalva class rocks (Ming et al., 2008; Morris et al., 2008) have haematite as the dominant Fe mineral phase. Elizabeth Mahon and Good Question class rocks are enriched in Si, depleted in Fe (Ming et al., 2008; Morris et al., 2008), and associated with the hot spring.

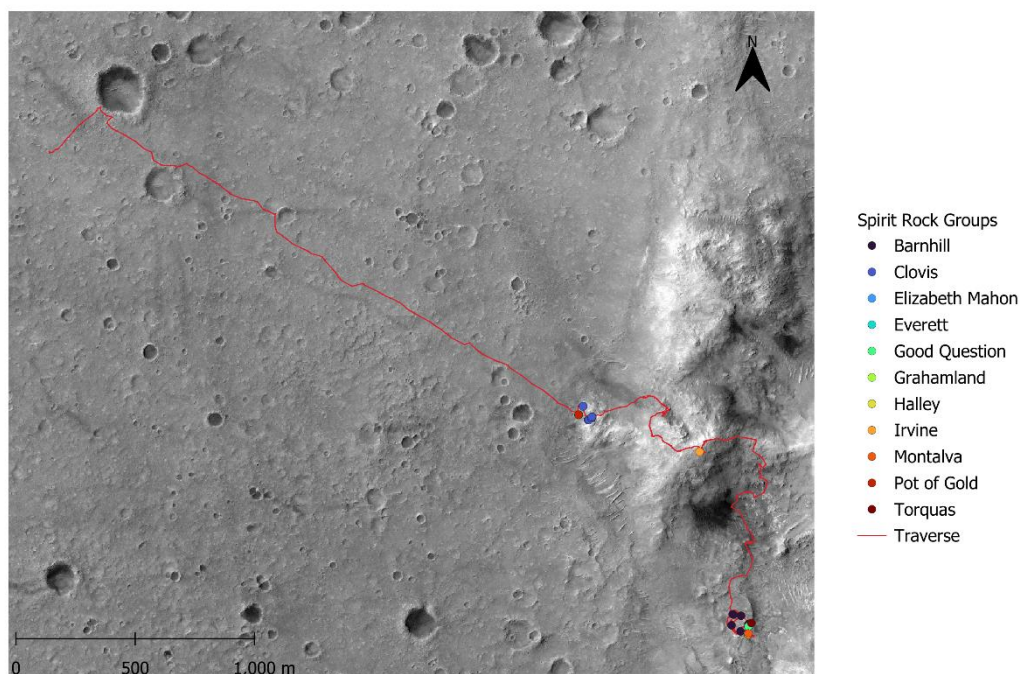


Figure 3.1 - Spirit rover traverse map with data acquisition points used in study shown

Meridiani Planum: Meridiani Planum was selected as the landing site for Opportunity because of a planet-wide uniquely strong haematite signal in Mars Global Surveyor Thermal Emission Spectrometer (TES) data. This signal stems from a lag deposit of haematite concretions – mm-sized spherules dubbed ‘blueberries’ - eroding out of a S-rich sedimentary sandstone, the Burns formation (Soderblom et al., 2004). The Burns formation is laterally extensive. Stratigraphic sections are exposed in a series of impact craters along Opportunity’s traverse, from its landing site in ~20 m diameter Eagle crater via ~150 m Endurance crater and ~220 m Erebus crater to ~750 m Victoria crater (Squyres et al., 2006b; Arvidson et al., 2011). They reveal a history of changing depositional environment alternating between dry and wet environments (Grotzinger et al., 2005; Metz et al., 2009). Sections of the stratigraphy show evidence of aeolian reworking after the initial deposition of the sandstone (Grotzinger et al., 2005). Throughout the Burns formation, diagenetic features such as mineral vugs, veins and haematite concretions are observed (McLennan et al., 2005). Lower, Middle, and Upper unit are exposed in Endurance crater and represent aeolian dune, aeolian sand sheet, and mixed aeolian sand sheet and interdune facies, respectively (Grotzinger et al., 2005). They are distinct in colour. All units contain evaporite minerals suggesting aeolian reworking material deposited under wet conditions. The Upper unit contains evidence for deposition in water where the water table had reached the surface (Grotzinger et al., 2005). The Whatanga contact separates Middle and Upper units and is a zone of diagenetic recrystallization (McLennan et al., 2005). The Upper unit corresponds to outcrop exposed at Opportunity’s landing site inside Eagle crater. Outcrop exposed at Erebus crater is topographically higher but tells the same story (Metz et al., 2005). The units Lyell, Smith and Steno (in order from lowest to highest stratigraphic layer) exposed at Victoria crater show a colour gradation similar to the Lower, Middle and Upper units at Endurance (Squyres et al., 2009).

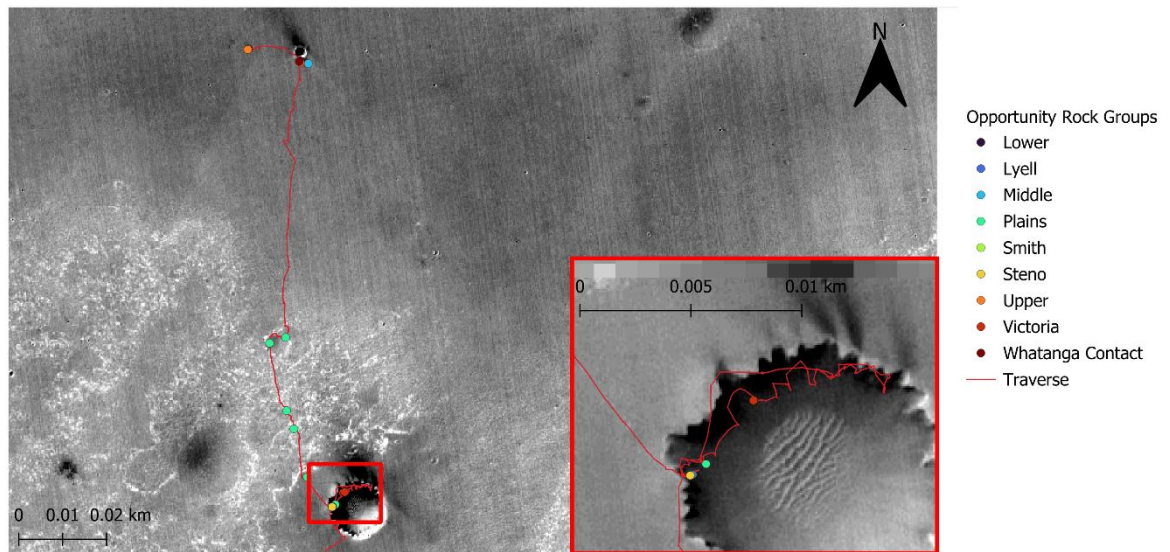


Figure 3.2 - Opportunity rover traverse with data acquisition points used in study shown

Gale crater: The Curiosity rover landed in ~155 km diameter Gale crater in the Aeolis quadrangle of Mars. This impact basin was selected as landing because of evidence that water would have flowed into it and because central Mount Sharp provides access to a succession of sedimentary layers. The evidence collected with Curiosity suggests alternating fluvial and lacustrine ancient environments (e.g. Bristow et al., 2021; Palucis et al., 2016; Rampe et al., 2017, 2020; Smith et al., 2021). The crater floor where Curiosity landed is covered by rocks of the Bradbury group (Rampe et al., 2017, 2020; Smith et al., 2021). Within this group, the rover observed coarse-grained sedimentary deposits, such as conglomerates and pebbly sandstones thought to be of fluvial origin. These coarser grained units are interspersed with mudstones of lacustrine origin which continue to become the dominant facies in the Murray formation once Curiosity started to ascend Mount Sharp. The Murray formation is unconformably overlain by an ancient aeolian dune field known as the Stimson formation which is thought to have undergone some form of diagenetic process leading to the formation of magnetite (Rampe et al., 2020). Other diagenetic features are observed throughout the stratigraphic section investigated with Curiosity. These features come in the form of various coloured veins, concretions, bleached zones and opaline silica (Bedford et al., 2019; Bristow et al., 2021; Payré et al., 2022; Rampe et al., 2017, 2020; Siebach et al., 2014). The timing of the diagenetic processes is still debated (Nachon et al., 2017); however, it does tell us that there was some form of

fluid movement through the sediment post deposition, and this can be seen within the geochemistry of the rocks.

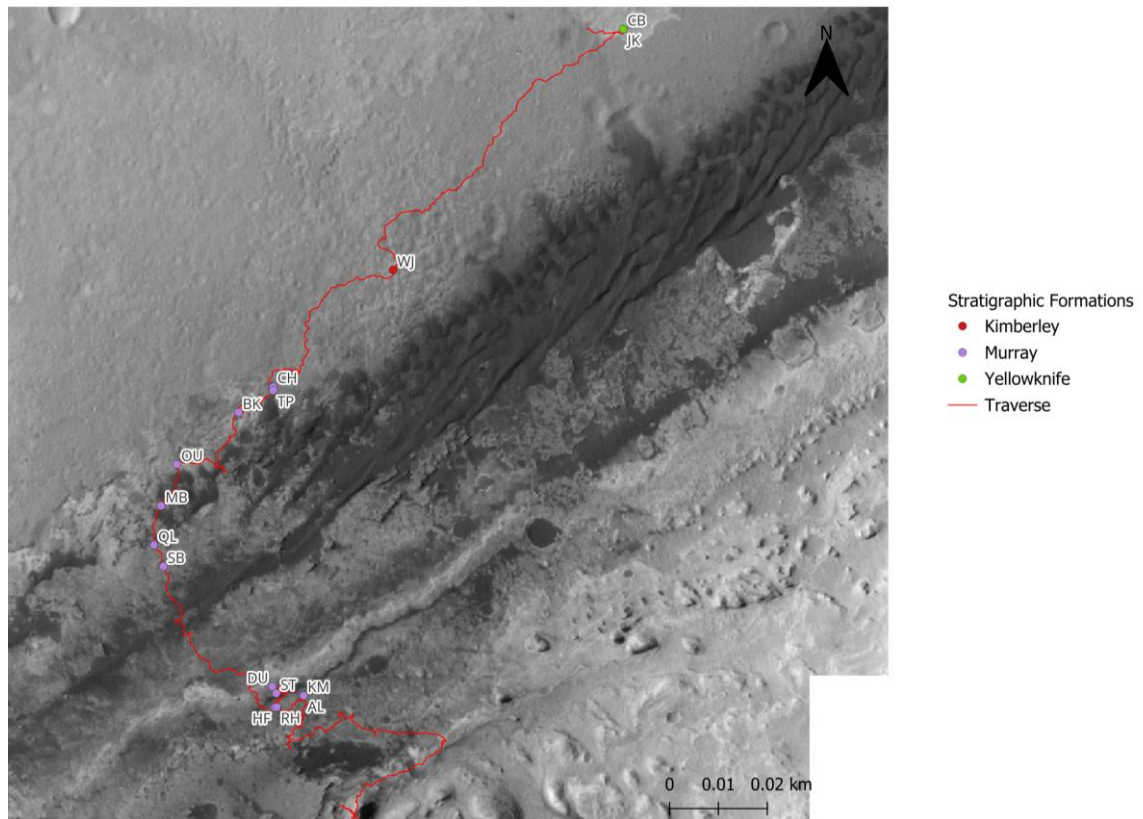


Figure 3.3 - Curiosity rover traverse with data acquisition points used in study shown. Labels correlate to core acronyms (Supplementary Information).

Target selection: Due to the sedimentary nature of reactive iron species, targets were selected based on whether they had a sedimentary origin and/or undergone some form of aqueous alteration. Soil, igneous, aeolian, most float rocks and meteorite measurements were not considered here.

The classification as sedimentary rock is based on measurements and images showing evidence of features such as a volatile-rich elemental composition (for example Cl), the presence of goethite, or crossbedding. From these distinctions, focus is placed on Clovis class rocks and rock classes at and around Home Plate in Gusev crater, the Burns formation at Meridiani Planum, and Bradbury Group and Murray formation in Gale crater. The Carolyn Shoemaker formation in Gale Crater has not been included because most of the drill core Fe-rich x-ray amorphous material percentages from that formation have yet to be published in the literature.

To fully identify the levels of aqueous alteration and subsequent diagenesis, an unaltered standard is needed. The Adirondack group of rocks from the Spirit rover traverse have been described as relatively unaltered (Morris et al., 2006a). Measurements from Adirondack group rocks were averaged and used as an unaltered standard within this study. Using the literature, measurements have been grouped based on rock classifications and units.

3.2.2. *Mineralogical datasets and reactive iron identification*

We used Mössbauer and CheMin mineralogical datasets to compare the amount of reactive Fe minerals with the amount of haematite. Haematite in this case is used as a proxy for the level of diagenesis experienced by the sedimentary rocks investigated. Haematite is the most thermodynamically stable Fe oxide, and diagenetic processes tend to transform the metastable reactive Fe minerals into haematite via dehydration and/or maturation (Bonsall et al., 2025; Posth et al., 2013; Schröder et al., 2016, 2025). However, reactive iron minerals can also include nanophase (<30 nm; also labelled superparamagnetic) haematite (Morris et al., 2006a, 2006b, 2008), which is distinct from well-crystalline haematite. Well-crystalline haematite is readily identified in Mössbauer and CheMin measurements, but nanophase haematite cannot be easily distinguished from other reactive Fe minerals. This distinction is important because they reflect different environments, where reactive iron is associated with more hydrated environments whilst well-crystalline haematite forms in periods of heating or high aridity (Cornell and Schwertmann, 2006).

In Gusev crater and at Meridiani Planum, mineralogy was determined with the Mössbauer spectrometers on board Spirit and Opportunity, respectively. Mössbauer spectroscopy measured Fe-bearing minerals only, which are quantified as the percentage of total Fe in the respective mineral phase. We use the data published by Morris and co-workers (Morris et al., 2006a, 2006b, 2008). In Gusev crater, Morris and co-workers (Morris et al., 2006a, 2008) assign the ferric Fe phase labelled Fe3D1 to npOx, which we equate with reactive Fe (Table 3.1). The Burns formation at Meridiani Planum contains a ferric phase with slightly different parameters labelled Fe3D3 (Morris et al. 2006b), which is unassigned but also consistent with npOx (Morris et al., 2006b) and used here as reactive Fe.

In Gale crater, mineralogy is determined with Curiosity's CheMin XRD channel. Mineral phases are quantified as wt%. All measurements contain a fraction of unidentified minerals labelled as X-ray amorphous (Rampe et al., 2017, 2020). These X-ray amorphous

phases contain Fe-rich, S-rich, and Si-rich materials (Smith et al., 2021). We equate the Fe-rich fraction (AmoFe) with reactive Fe (Table 3.1).

It must be noted that the Mössbauer spectrometers and the APXS instruments are so-called contact instrument, i.e. they are placed in contact with or close proximity of a martian surface target without any further need for sample preparation. The CheMin instrument on the other sits inside the body of the curiosity rover and requires the collection of drill cores and processing of these cores into a powder. As a result, there are Almost as many Mössbauer measurements as APXS measurements, but there are far fewer CheMin measurements compared to APXS measurements.

To be able to compare the amount of reactive Fe between the three landing sites, we need to turn the abundance of npOx and AmoFe into mineral wt. %. We use the elemental chemistry measured with the APXS on board all three rovers for the necessary calculations. Weight percentages for npOx and well-crystalline haematite in Gusev crater and at Meridiani Planum were calculated via Equation 1 using the percentages of total Fe in the respective mineral phases measured with Mössbauer spectroscopy and the amount of Fe given as FeO_T measured with the APXS on the same target (Table S1).

$$Target\ mineral\ wt.\ \% = \frac{(target\ mineral\ MIMOS\ II\ \%)\times(APXS\ elemental\ oxide\ \%)}{100} \quad (1)$$

Equation 2 was applied to to calculate the wt. % of AmoFe, using total iron oxide X-ray amorphous components (FeO_{TAmC}) and the total amount of X-ray amorphous components (AmC). Haematite wt. % were already provided in Smith et al., 2021 from mass-balance calculations.

$$AmoFe\ wt.\ \% = \frac{(FeO_{TAmC})\times(total\ AmC)}{100} \quad (2)$$

3.2.3. Geochemical datasets

Elemental chemistry at all three landing sites was measured with APXS instruments on board Spirit, Opportunity and Curiosity. We use elemental oxide data available via the Planetary Data System (PDS) (Berger, 2022; Gellert, n.d.). While FeO_T was used to enable a quantitative comparison of npOx and AmoFe across the three landing sites, FeO_T, Al₂O₃ and SiO₂ are used to constrain diagenetic processes. In the absence of free oxygen, FeO dissociates at circumneutral pH into its constituent ions: Fe²⁺ and O²⁻ (Beveriskog and Puigdomenech, 1996), whereas Al₂O₃ only dissociates at acidic pHs below 4 (Zhu and Hihara, 2010). This dissociation causes the constituent ions to become mobile, and

fractionation of the elements thus helps to constrain water-to-rock ratios and pH. FeO_T , Al_2O_3 and SiO_2 are plotted onto ternary diagrams using the ggtern package in Rstudio (Hamilton and Ferry, 2018).

3.2.4. *Organic carbon dataset*

Only the Curiosity rover investigating Gale crater is equipped with an instrument, SAM, that can measure organic carbon. Like CheMin, it sits inside the body of Curiosity and requires processed drill core samples. The focus so far has been on the identification of individual organic compounds with GCMS (Eigenbrode et al., 2018; Freissinet et al., 2015, 2025; Millan et al., 2022). A full quantification of carbon was only performed for the Cumberland mudstone sample, collected from the Sheepbed member of the Yellowknife Bay formation in the Bradbury group, by stepped heating combustion (Stern et al., 2022). We therefore cannot compare the presence of reactive Fe minerals with the presence of organic carbon compounds in a systematic way. Instead, we use the qualitative data from the published results to feed into our discussion.

3.4. Results

3.4.1. Gusev crater

Figure 3.4 shows a ternary diagram for element oxide abundances of SiO_2 , FeO and Al_2O_3 for different rock classes in Gusev crater as measured with Spirit's APXS. The rock classes Barnhill, Clovis, Halley and Torquas cluster closely together and show a trend of FeO loss at relatively stable Al_2O_3 relative to Adirondack (Trend 2 in Figure 3.4 – all trend lines are summarized in Table 3.2). Because low water-to-rock ratios would result in isochemical

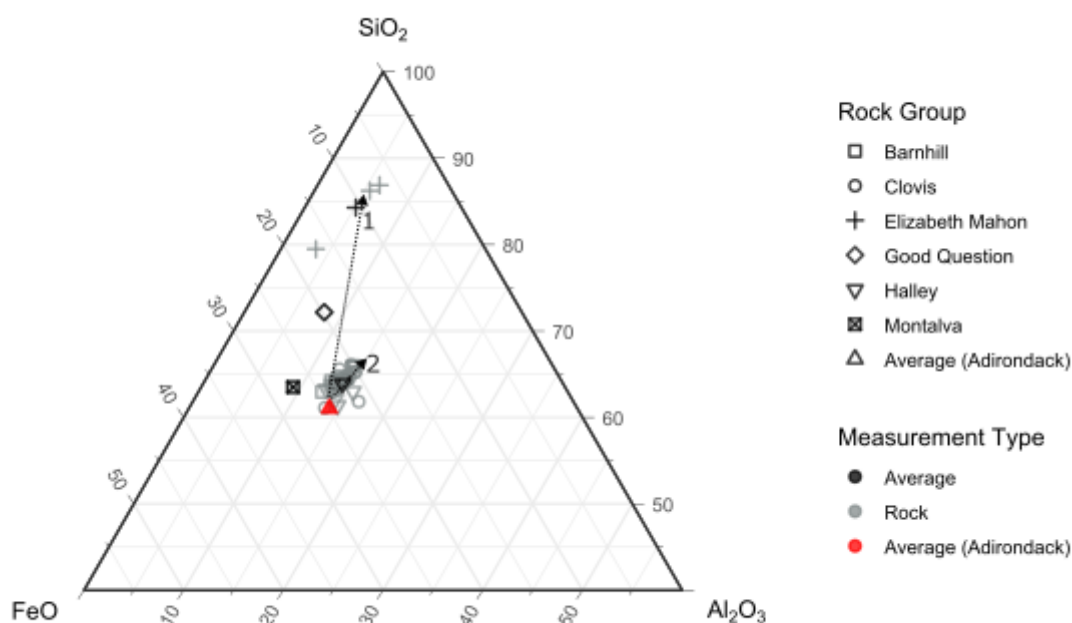


Figure 3.4 - SiO_2 - FeO - Al_2O_3 ternary diagram showing composition of selected Gusev Crater rocks. Observed trends are denoted with black arrows and labelled numerically.

alteration, this suggests alteration by an aqueous fluid at circumneutral pH with high water-to-rock ratios. Rock classes Good Question and Elizabeth Mahon show a loss of both FeO and Al_2O_3 and an increase in SiO_2 relative to Adirondack (Trend 1 in Figure 3.4), suggesting alteration by acidic aqueous fluids at high temperatures and high water-to-rock ratios.

In Figure 3.5, npOx is plotted against haematite to assess the organic carbon preservation potential of the investigated rock classes. The preservation potential is highest where npOx abundances are high and haematite abundances - as our proxy for the level of diagenesis - are

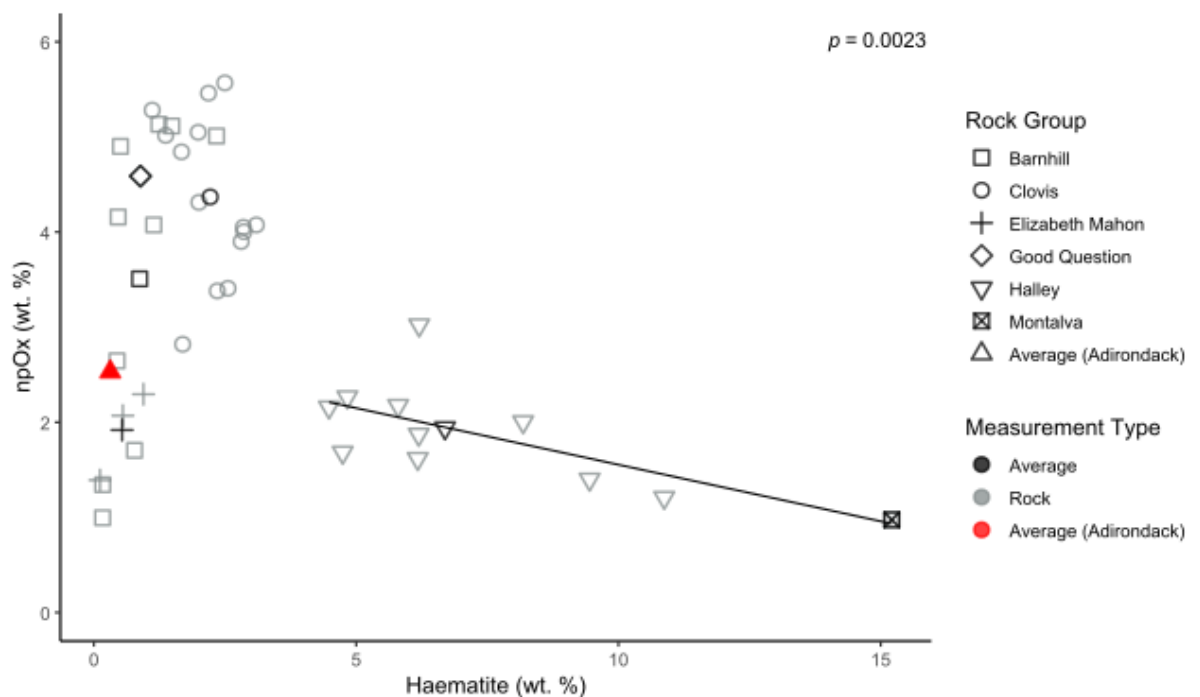


Figure 3.5 - Graph showing the relationship between haematite and npOx composition of selected Gusev Crater rocks. Linear model trend lines are displayed for samples for samples with >4 wt. % haematite (black line). The associated p value of 0.0023 is shown.

low. Members of the Barnhill and Clovis rock classes show a high preservation potential. Halley and Montalva rock classes on the other hand show a strong correlation between npOx loss and haematite gain, i.e. the transformation of reactive Fe minerals into well-crystalline haematite, demonstrating poor preservation potential and a high level of diagenesis.

3.5. Meridiani Planum

Figure 3.6 shows a ternary diagram for element oxide abundances SiO_2 , FeO and Al_2O_3 for different rock groups at Meridiani Planum as measured with Opportunity's APXS. All rock groups shown are subgroups of the Burns formation and cluster closely together. FeO values range from decrease to increases relative to Adirondack but a consistent decrease in Al_2O_3 . If increases in FeO are interpreted to result from a higher abundance of haematite concretions in the instrument field of view, this suggests alteration by low pH aqueous fluids. The occurrence of jarosite throughout the Burns formation confirms that because

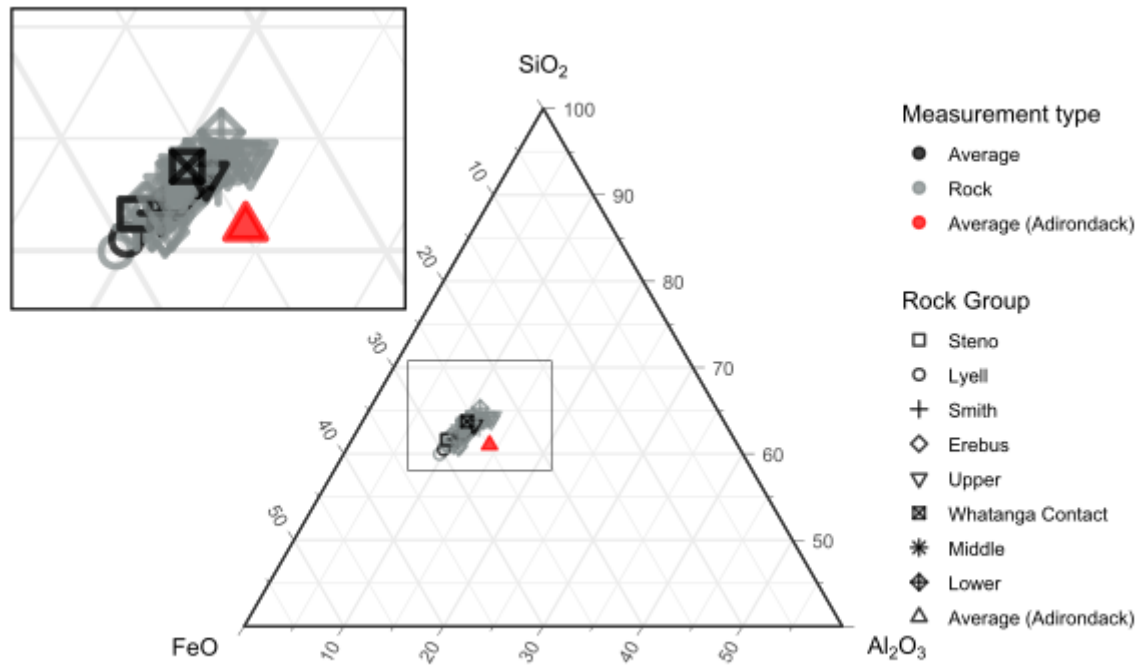


Figure 3.6 - $\text{SiO}_2\text{-FeO-Al}_2\text{O}_3$ ternary diagram showing composition of selected Meridiani Planum rocks.

this mineral only forms at low pH (Klingelhöfer et al., 2004). In the absence of any intense SiO_2 enrichment, the alteration was not due to a high temperature environment.

There is little variation in npOx versus haematite within the samples analysed by the Opportunity rover (Figure 3.7). Generally elevated values of haematite and the diagenetic formation of haematite concretions speak for a low organic carbon preservation potential.

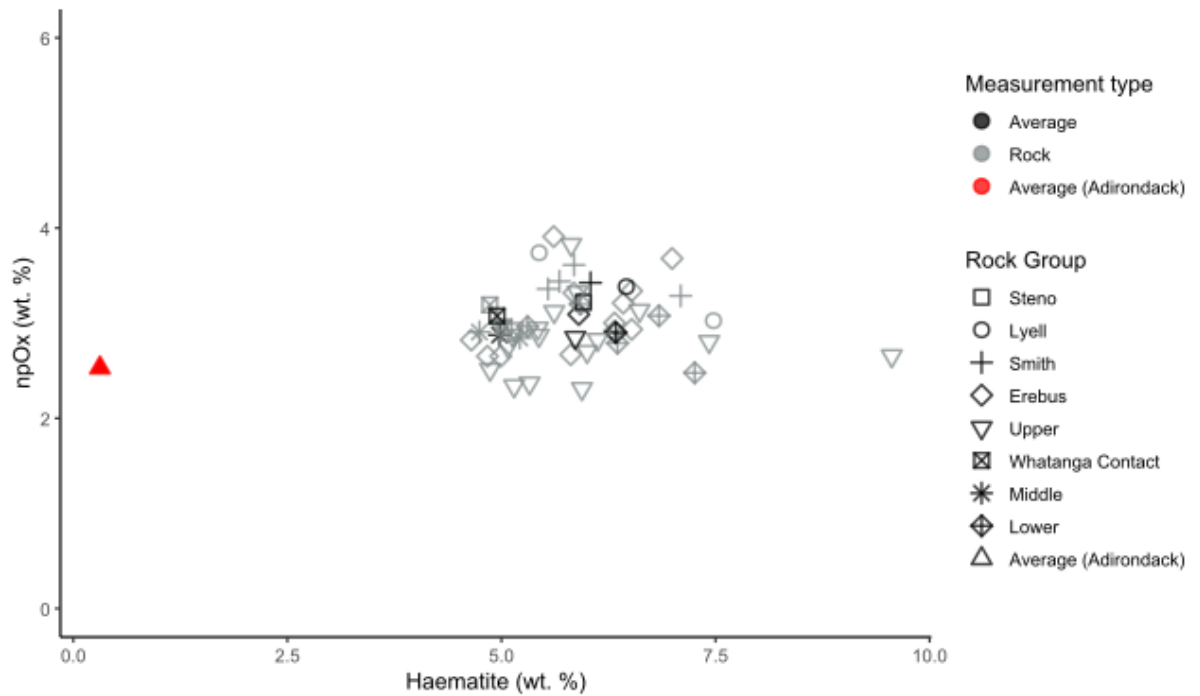


Figure 3.7 - Graph showing the relationship between haematite and npOx composition of selected Meridiani Planum rocks.

3.6. Gale crater

Figure 3.8 shows a ternary diagram for element oxide abundances SiO_2 , FeO and Al_2O_3 for different rock groups in Gale crater as measured with Curiosity's APXS. The plot reveals distinct geochemical trends for Bradbury group rocks compared the Murray formation on Mount Sharp. Looking at the Bradbury group rocks in more detail (Figure 3.9) shows a linear trend. While targets in the Yellowknife Bay and the Kimberley formations are enriched in FeO and depleted in both Al_2O_3 and SiO_2 relative to Adirondack, Other Bradbury group rocks show the opposite behaviour. This suggests alteration to have occurred in a closed system, which is consistent with Gale crater not having an outlet channel (Palucis et al., 2016). In this closed system, Fe would have been removed from the Other Bradbury rocks, resulting in relatively higher Si and Al abundances. The removed Fe was then deposited in the Yellowknife Bay and Kimberley formations. A relative lack of haematite within the Bradbury group (Figure 3.11) suggests there was no stage of evaporation or heating to cause dehydration to form haematite (McLennan et al., 2014).

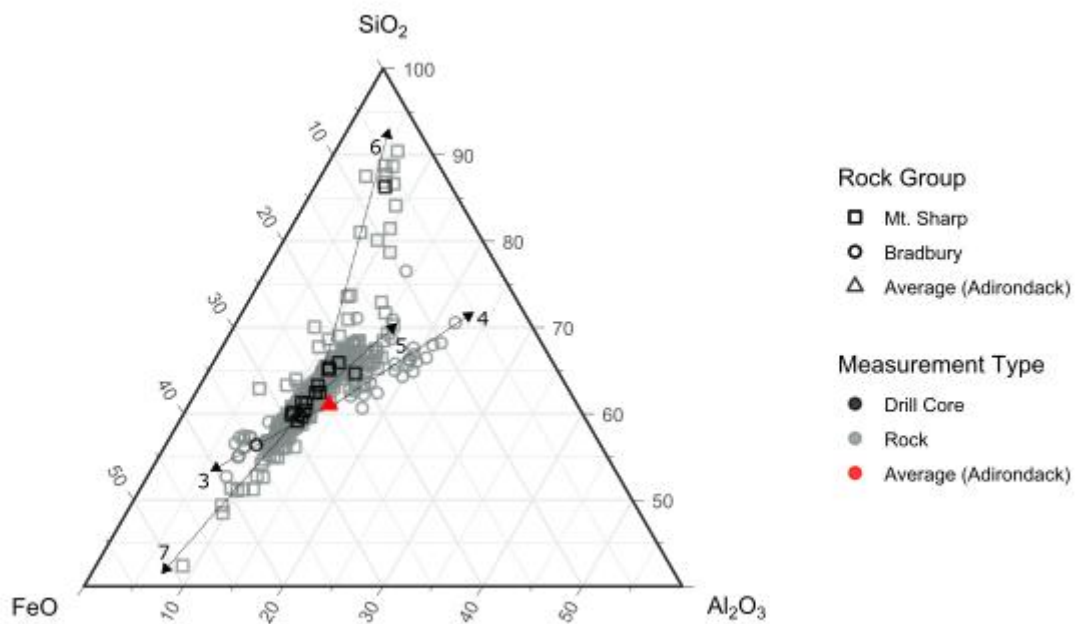


Figure 3.8 - $\text{SiO}_2\text{-FeO-Al}_2\text{O}_3$ ternary diagram showing composition of selected Gale Crater rocks. Observed trends are denoted with black arrows and labelled numerically.

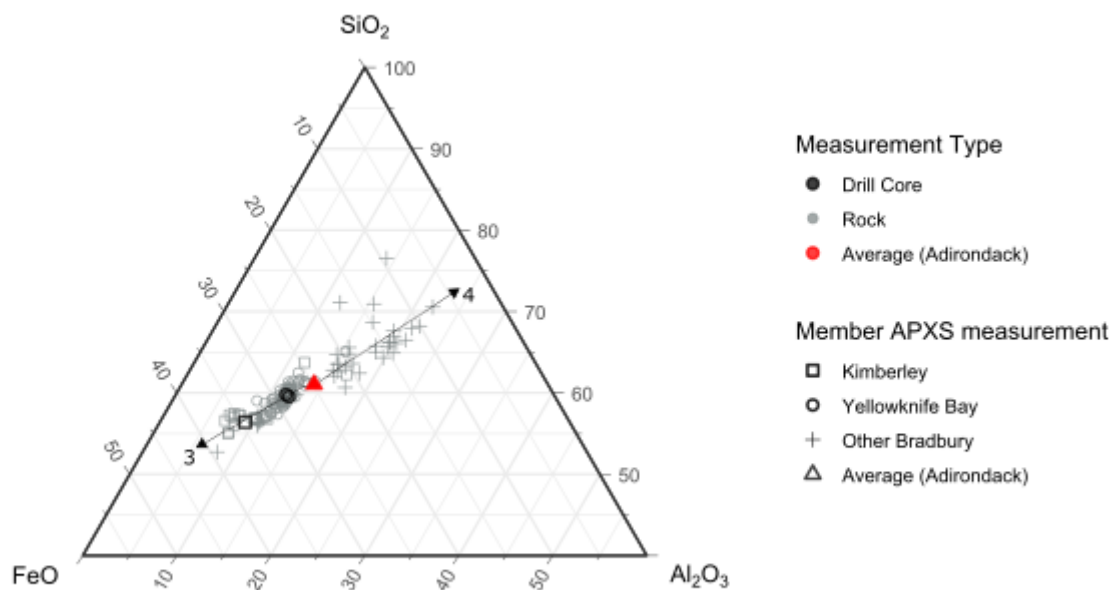


Figure 3.9 - $\text{SiO}_2\text{-FeO-Al}_2\text{O}_3$ ternary diagram showing composition of selected Bradbury Group rocks. Observed trends are denoted with black arrows and labelled numerically.

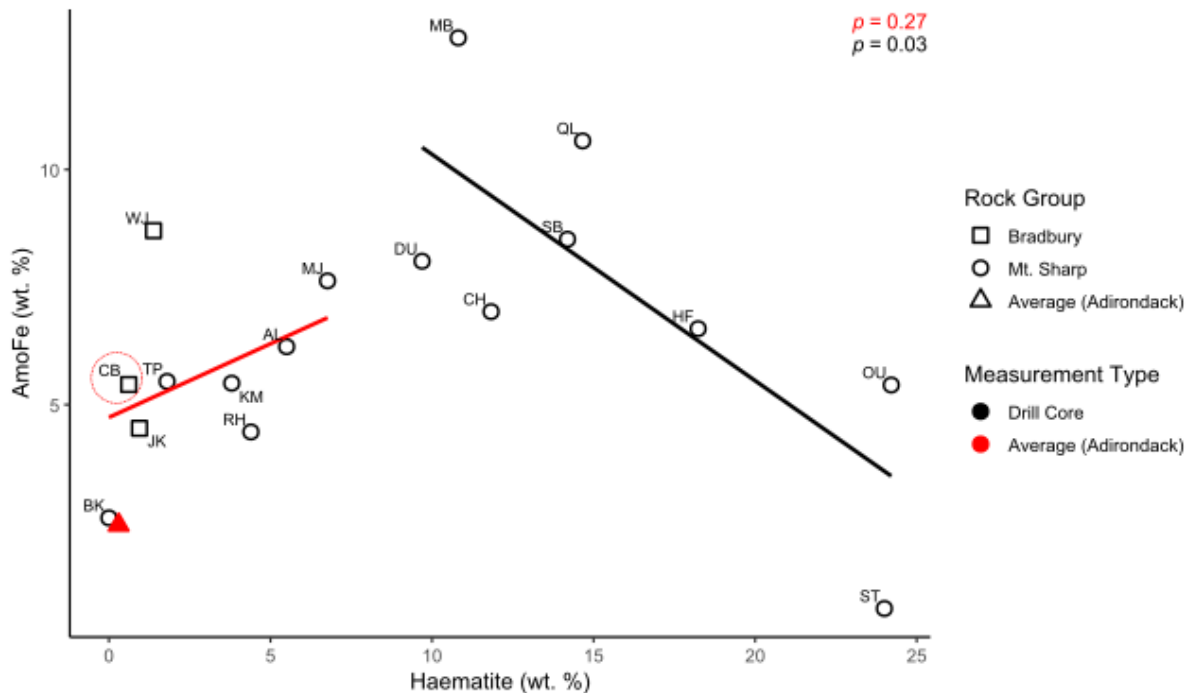


Figure 3.11 - Graph showing the relationship between haematite and npOx composition of selected Gale Crater rocks. Linear model trend lines are displayed for samples with <9 wt. % haematite (red line) and samples for samples with >9 wt. % haematite (black line). Associated p values are shown with text colour corresponding to the same colour line (0.27 and 0.03 respectively). Labels correlate to core acronyms (Supplementary Information).

Taking a closer look at the Murray formation targets (Figure 3.10), shows a similar albeit not parallel trend. Iron is removed from the Jura and Blunts Point members of the Murray formation and deposited in the Sutton Island and Pettegrove Point members. Targets of the Pahrump Hills member branch off this main trend near the centre of the diagram,

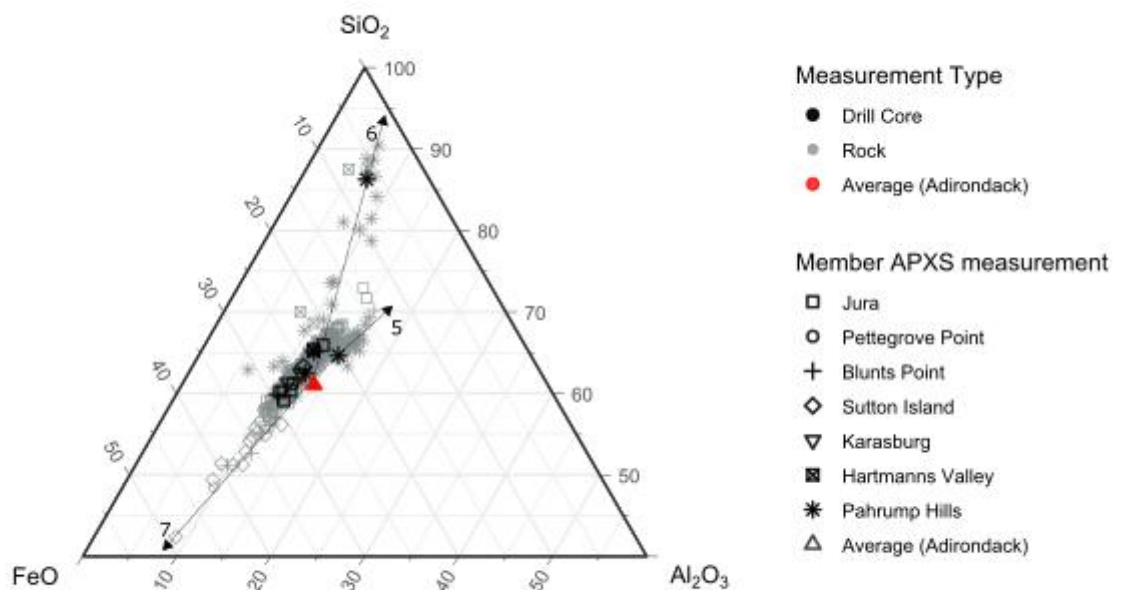


Figure 3.10 - SiO₂-FeO-Al₂O₃ ternary diagram showing composition of selected Murray Formation rocks. Observed trends are denoted with black arrows and labelled numerically.

showing a loss in FeO and an increase in both SiO₂ and Al₂O₃. This suggests circumneutral fluid alteration occurred to mobilise FeO within the Pahrump Hills member and to an extent, the Jura, and Blunts Point members (all mudstone members within the Murray Formation).

A second trend within the Pahrump Hills member targets shows the loss of both FeO and Al₂O₃ resulting in strong enrichment in SiO₂. This suggests that a high temperature process effected the sediment at some point in its history. Measurements by the CheMin instrument show the presence of high temperature polymorphs of quartz, such as tridymite, within the Buckskin (BK) drill core from the Pahrump Hills member (Morris et al., 2016; Rampe et al., 2017, 2020). Whilst still being debated, the general consensus is that this is due to pyroclastic input by silicic volcanism either directly or recycling into the crater from the rim (Morris et al., 2016; Payré et al., 2022). Comparing amounts of AmoFe and haematite within the Buckskin drill core with the unaltered average shows very little difference, reinforcing a more volcanic origin with no post deposition change in the iron mineralogy.

APXS measurements from Hartmanns Valley also shows an increase in SiO₂, along with a decrease in FeO and Al₂O₃. The Oudam (OU) drill core came from this formation and shows a high wt. % of haematite. This indicates heating of the sediment, which was likely linked to the volcanic activity that occurred during the deposition of Pahrump Hills.

Unlike the trend in the Bradbury group, the trends in the Murray formation do not overlap with Adirondack. This suggests a different sediment source for Bradbury Group and the Murray formation on Mount Sharp (Siebach, 2016) that was subject to widespread diagenetic processes. The deposition of the top of the Bradbury group layers and the bottom of the Murray formation layers occurred concurrently with each other with different input sources, resulting in an interfingering contact between the Bradbury group and the Murray formation (Bedford et al., 2019; Grotzinger et al., 2015; Rampe et al., 2017; Siebach, 2016).

Plotting AmoFe against haematite in Figure 3.11 shows an overlapping range of AmoFe abundances for both Bradbury group and Murray formation targets. However, the Bradbury group targets contain very little haematite and have thus a higher preservation potential than the Murray formation targets, which contain a larger range of haematite abundances.

Table 3.2 - Summary of trends observed by MER and MSL rovers.

Trend	Characteristics			Process	Environment
	FeO _T	Al ₂ O ₃	SiO ₂		
1	Decrease	Decrease	Increase	Hot acidic fluid movement	Acidic hot spring
2	Decrease	Stable	Increase	Circumneutral fluid movement	
3	Increase	Decrease	Decrease	Acidic fluid movement	Fluvial/Lacustrine
4	Decrease	Increase	Increase	Acidic fluid movement	Closed basin
5	Decrease	Increase	Increase	Circumneutral fluid movement	fluvial/lacustrine
6	Decrease	Decrease	Increase	High temperatures Fe-enriched fluid movement	Silicic volcanic input
7	Increase	Decrease	Decrease	High temperatures Fe-enriched fluid movement	Silicic volcanic input Fluvial/Lacustrine

3.5. Discussion

3.5.1. Implications for organic carbon preservation

On Earth, more than 20 % of organic carbon stored in sediments are directly bound to reactive Fe minerals. The storage of organic carbon does not depend on the presence of reactive Fe minerals alone but also on the depositional environment and the quality and sources of organic carbon compounds. Though there is no direct correlation between the amount of reactive iron in sediments and the amount of organic carbon stored, the presence of reactive Fe minerals in sedimentary rocks on Mars does enhance their preservation potential. Because reactive Fe minerals are metastable and would transform into more thermodynamically stable minerals such as well-crystalline haematite upon higher degrees of diagenetic alteration, their presence on Mars further indicates that

diagenetic processes were limited. This further enhances the potential for the preservation of organic carbon compounds. Here we have demonstrated the presence of reactive Fe minerals on Mars and used it together with the amount of well-crystalline haematite as a proxy for the degree of diagenesis to assess the preservation potential of sedimentary rocks at three rover landing sites. Comparing the landing sites in Figure 7 shows that sedimentary rocks at Gale crater have the highest preservation potential, i.e. they have the highest amounts of reactive Fe (in the form of AmOFe) combined with the lowest amount of haematite. The Burns formation at Meridiani Planum exhibits the lowest preservation potential. Rock classes in Gusev crater show a mix of high and low preservation potentials.

Burns formation targets show consistent evidence of diagenetic processes indicating interaction with an acidic fluctuating water table (McLennan et al. 2005). While such an aqueous system may have been habitable, it would have challenged prebiotic reactions though to be important for the origin of life (Knoll et al., 2005), and the conditions are not in favour of preserving organic compounds. The Fe₃D₃ phase we have equated with npOx may be mostly haematite. Burns formation rocks contain more haematite than present in the well-crystalline haematite concretions, and the Fe₃D₃ phase may be nanophase or superparamagnetic haematite for the most part (Fleischer et al., 2010).

At Gale crater, the Cumberland (CB) drill target was taken from a mudstone in the Yellowknife Bay formation of the Bradbury group. It has a moderately high amount of reactive Fe compared to other samples in Gale crater stemming from the Murray formation but contains hardly any well-crystalline haematite. Its reactive iron content is higher than all targets in the Burns formation and as high as the highest amounts in Gusev crater rock targets. SAM analyses of Cumberland have identified aromatic and aliphatic compounds including long-chain alkanes (Freissinet et al., 2015, 2025). The drill targets Mojave (MJ) and Confidence Hills (CH) have higher amounts of reactive Fe but also contain enhanced levels of hematite. SAM measurements identified thiophenes as well as aromatic and aliphatic organic compounds (Eigenbrode et al., 2018).

Barnhill and specifically Clovis class rocks in Gusev crater are of high interest because they have reactive Fe amounts comparable to the Cumberland drill core as well as low haematite levels. Clovis class rocks potentially contain clay minerals (Ruff et al., 2006; Wang et al., 2006). The Elizabeth Mahon rock class associated with the hot spring system take on their own significance because silica is good at preserving biosignatures

independent of the presence of reactive iron. They also have low levels of haematite. In fact, the morphology of hot spring deposits at Home Plate has been touted as a biosignature in itself (Ruff and Farmer, 2016).

3.5.2. Implications for organic carbon measurements

While the presence of reactive iron minerals enhances the preservation potential of sedimentary rocks for organic carbon, it poses a challenge for measuring and accurately identifying these organic carbon compounds. To measure organic carbon compounds, they have to be released into a gas phase, which generally happens via pyrolysis or laser desorption. The amount of heat added this way also facilitates reactions between reactive Fe minerals and organic carbon (Posth et al., 2013; Schröder et al., 2016). It has been shown that the presence of iron minerals during pyrolysis can reduce the detectability of certain organic compounds, but this effect depends on the specific iron minerals present and is mitigated in the presence of clay minerals (Royle et al., 2021; Tan et al., 2021). The effect is lowest in the presence of haematite because haematite cannot dehydrate and because haematite is the most thermodynamically stable Fe oxide and is therefore less prone to play a part in redox reactions with organic matter. It is thus important to know what minerals are present as reactive Fe minerals. But our results above show that this is challenging in itself, even on Earth (e.g. Hepburn et al., 2020).

The Perseverance rover and the future Rosalind Franklin rover use Raman spectroscopy for mineral identification and carbon characterization. However, Raman lasers themselves provide enough energy to dehydrate reactive iron minerals and transform them into haematite (Bonsall et al. 2022; Schröder et al. 2025). They may thus provide a false detection of haematite, which would be less concerning for carbon volatilization via pyrolysis or laser desorption.

Rocks providing other means of carbon conservation may seem easier to investigate under these circumstances, e.g. the high silica hot spring deposits in Gusev crater. However, the Martian crust is enriched in Fe relative to Earth, and Fe-rich sedimentary rocks are therefore the norm on Mars. It is important to find ways to characterize reactive Fe minerals and to understand their effect on organic carbon measurements in situ on Mars, e.g. with MOMA on the future Rosalind Franklin rover, or in the laboratory on samples returned from Mars.

4. Conclusions

We have demonstrated the presence of reactive Fe minerals on Mars. We used the amount of reactive Fe versus the amount of well-crystalline haematite as a proxy for the degree of diagenetic alteration to assess the organic carbon preservation potential of sedimentary rocks in Gusev crater, at Meridiani Planum and in Gale crater. Sedimentary rocks in Gale crater have the highest preservation potential, and organic carbon has been identified in these rocks. This demonstrates that we can use the same assessment to guide current and future rover missions to areas with enhanced preservation potential, for example when selecting a drill site for the future Rosalind Franklin rover.

However, reactive Fe minerals also pose a challenge for the measurement of organic carbon because they can react with organic carbon when energy is provided via pyrolysis or laser desorption. The extent of this effect depends on which Fe (hydr)oxides are actually present. Determining this iron mineralogy is also a challenge. Raman lasers, for example, can dehydrate reactive minerals resulting in a false haematite detection. These effects need to be investigated further to provide an accurate inventory of organic carbon compounds identified with current and future missions and in returned samples.

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4. Raman spectroscopy of iron oxides

4.1. Introduction

Raman spectroscopy is a technique that utilises Raman scattering to identify both minerals and organic molecules. Currently, Nasa's Mars 2020 rover, *Perseverance*, is exploring the Martian surface with 2 Raman spectrometers onboard: SuperCam and Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals (SHERLOC). SuperCam is able to receive the Raman signal from a distance of up to 12 m away from the sample, whilst SHERLOC uses fine-scale imaging. The future ESA ExoMars rover, *Rosalind Franklin*, also has a Raman spectrometer as a part of its payload: the Raman Laser Spectrometer (RLS).

Certain minerals are known to fluoresce a lot due to laser excitation, causing difficulty in phase identification. Iron oxides are one such group known to fluoresce a lot under laser excitation. To avoid this, either a larger wavelength laser is needed (for example 785 nm over 532 nm) or longer acquisitions are needed. However, studies have found that the laser used to induce Raman scattering can dehydrate iron oxides into haematite (Hanesch, 2009), which is seen in Chapter 5. Longer acquisition times increases the potential of damage occurring but if the acquisition time is not long enough then the spectrum is difficult to interpret. On the Martian surface where iron oxides are abundant, this can cause problems with data gathering and interpretation. Further to this, it is unknown how this dehydration reaction will affect nanophase iron oxides (npOx) and any bound organic matter. Whilst the *Perseverance* rover has been successful in identifying iron oxides on the Martian surface, the exact mineralogy has not been identified (Corpolongo et al., 2023).

In this study, a RLS simulator is used to analyse different iron oxides of different grain sizes to begin to understand the parameters needed to analyse these on the Martian surface without causing damage. Following this, some samples were analysed with a 785 nm (red) Raman spectrometer to aid in the identification of haematite in potentially laser damaged samples.

4.2. Raman Spectrometers on Mars

4.2.1. SuperCam Raman Spectrometer

The SuperCam Raman Spectrometer uses a pulsed laser that is also used for Laser-Induced Breakdown Spectroscopy (LIBS). The laser uses a wavelength of 532 nm (green) to observe Raman bright-minerals and organics from up to a distance of ~7 m away. Measurements are taken in 100-200 laser shots at the sample which are then averaged on board as no damage to the sample should occur due to the laser. Measurements are taken within the Raman region of 535-7,070 cm^{-1} (Wiens et al., 2021).

4.2.2. Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals (SHERLOC)

The SHERLOC instrument uses a pulsed deep UV laser with a wavelength of 248.6 nm which views minerals and organics from ~48 mm away from the target. These measurements are mapped and overlaid with context images from the Wide Angle Topographic Sensor for Operations and eNginEering (WATSON). 2,000 laser pulses are used for measurement point. Measurements are taken in the Raman region of 800-4,000 cm^{-1} with particular focus on identification of organics (Bhartia et al., 2021).

4.2.3. Raman Laser Spectroscopy (RLS)

The RLS instrument uses a pulsed laser with a wavelength of 532 nm (green) to investigate a spot size of ~50 μm . RLS will analyse powdered samples obtained by the drill onboard the ExoMars rover with context images taken by the Close-UP Imager (CLUPI) instrument also a part of the payload. Measurements are taken in the Raman region of 0-4,000 cm^{-1} (Rull et al., 2017).

4.3. Materials

A selection of both natural and synthetic iron oxides are presented here, having been analysed with Raman spectroscopy to understand the effects of laser induced damage and how to prevent this (Table 4.1). Natural samples of smaller grain sizes were prepared by manually crushing a portion of the natural sample with a hammer, grinding with a pestle and mortar then sieved to get the desired size.

Table 4.1 - Mineral, grainsize and Raman wavelength used

Mineral	Grain Size	Raman Wavelength (nm)
Synthetic akaganeite	Powder	532
Synthetic lepidocrocite	Powder	532
Synthetic magnetite	Powder	532
Iridescent goethite	Hand specimen (natural sample)	532
Natural goethite	Hand specimen (standard and natural sample)	532
	>500 μm	785
	<63 μm	785 and 532
Synthetic goethite	Powder	532
Natural haematite	>500 μm (standard)	785

4.4. Methodology

See Chapter 2 for exact Raman spectroscopy set up.

Table 4.2 contains the strongest, common Raman bands used for mineral identification of iron oxides. These bands are also used to identify damage occurring to the sample due to the laser.

Table 4.2 - Characteristic Raman peaks of selected iron oxides

Mineral	Formula	Key Peaks ¹
Akaganeite	$\beta\text{-FeOOH}$	380
Feroxyhyte	$\delta\text{-FeOOH}$	392 666
Ferrihydrite 2- line	Fe(OH)_3	710
Ferrihydrite 6-line	Fe(OH)_3	370 710
Green rust	Fe(OH)_2	550
Goethite	$\alpha\text{-FeOOH}$	300 386
Haematite	$\alpha\text{-Fe}_2\text{O}_3$	226 292 411 1320
Lepidocrocite	$\gamma\text{-FeOOH}$	252 528
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$	381 718
Magnetite	Fe_3O_4	667
Schwertmannite	Hydrated iron sulphate	421
Wuestite	FeO	600

¹Cornell and Schwertmann, 2006

4.5. Results

4.5.1. Akaganeite

532 nm Raman spectroscopy of synthetic akaganeite show the characteristic peak at 380 cm^{-1} (Figure 4.1). Acquisitions 1, 2 and 5 produced noisy spectra with no visible peaks.

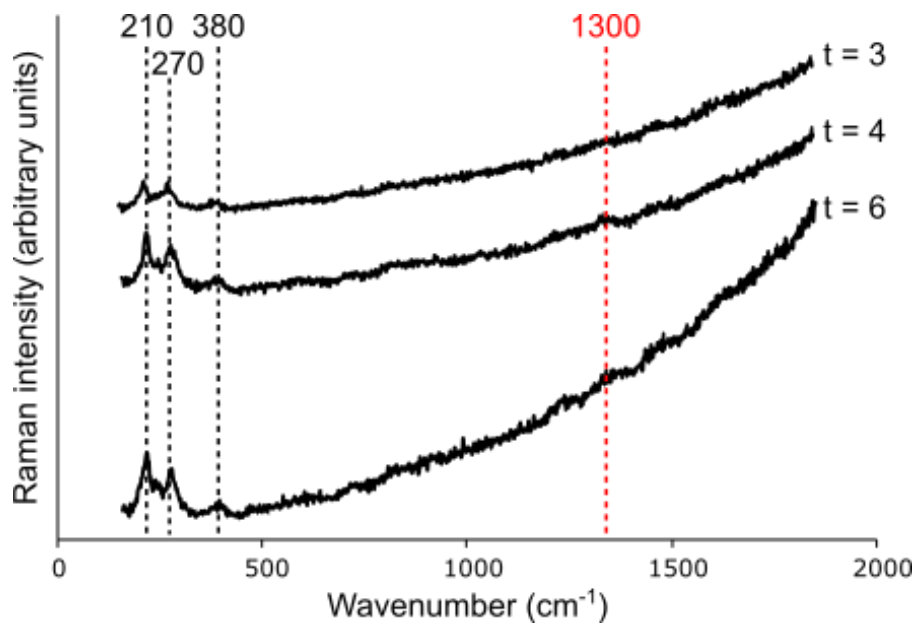


Figure 4.1 - 532 nm Raman spectra of synthetic akaganeite powder over time. Peaks at 210, 270, 380 cm^{-1} are indicated with black dotted lines. The haematite peak at 1300 cm^{-1} is indicated with a red dotted line. t denotes spectrum collection order.

Peaks at 210 and 270 cm^{-1} are also present in the spectra which are assignable to any iron oxide peak (Table 4.2). These peaks are likely due to either contamination or the presence of

jarosite, which akaganeite exists in equilibrium with

(Zhang et al., 2024). Fluorescence of the sample is seen with the increase in gradient of the spectra at $t = 6$ compared to $t = 3$ and $t = 4$. This makes identification of dehydration to haematite difficult to observe.

4.5.2. Lepidocrocite

532 nm Raman spectroscopy of lepidocrocite reveals a peak at 249 cm^{-1} (Figure 4.2) which is within the range for the characteristic peak of 252 cm^{-1} assigned to lepidocrocite (Table 4.2). Over time, as the sample is subjected to the laser for longer periods of time, a wide peak at 1300 cm^{-1} appears which is characteristic the presence of haematite within the sample. The peak at 249 cm^{-1} is not fully seen until haematite becomes present within the spectra.

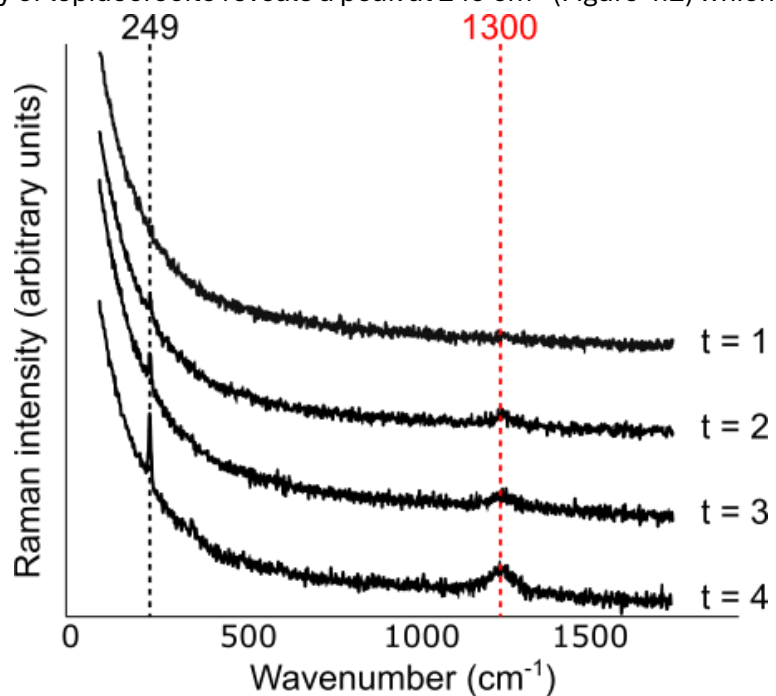


Figure 4.2 – 532 nm Raman spectra of synthetic lepidocrocite powder over time. The peak at 249 cm^{-1} is indicated with a black dotted line. The haematite peak at 1300 cm^{-1} is indicated with a red dotted line. t denotes spectrum collection order.

4.5.3. Magnetite

532 nm Raman spectroscopy was unable to identify any peaks, resulting in very noisy spectra. The dark colour of the magnetite powder likely caused most of the laser energy to be absorbed and not emitted so no peaks were observed.

4.5.4. Goethite

532 nm Raman Spectroscopy

785 nm Raman spectroscopy of different goethite samples revealed peaks that can be assigned to either goethite or haematite.

Iridescent goethite (t_{iri}) is a mixture of both haematite and goethite naturally. Raman analysis of the sample however only revealed peaks characteristic of haematite, not goethite (Figure 4.3).

Raman analysis of the natural sample with a grain size below $63\ \mu\text{m}$ ($t_{<63\ \mu\text{m}}$) shows peaks characteristic of haematite. The spectrum shows a high amount of fluorescence from the sample, potentially obscuring peaks $>500\ \text{cm}^{-1}$ (Figure 4.3).

The hand specimen standard (t_{stan}) shows peaks belonging to both haematite and goethite (Figure 4.3).

The synthetic goethite powder spectrum (t_{syn}) shows peaks belonging to goethite; however, the wide $1300\ \text{cm}^{-1}$ band characteristic of haematite is present (Figure 4.3).

Raman spectroscopy of a natural goethite hand specimen (t_{nat}) does not show haematite peaks, however peaks $<500\ \text{cm}^{-1}$ are somewhat obscured by fluorescence from the sample (Figure 4.3).

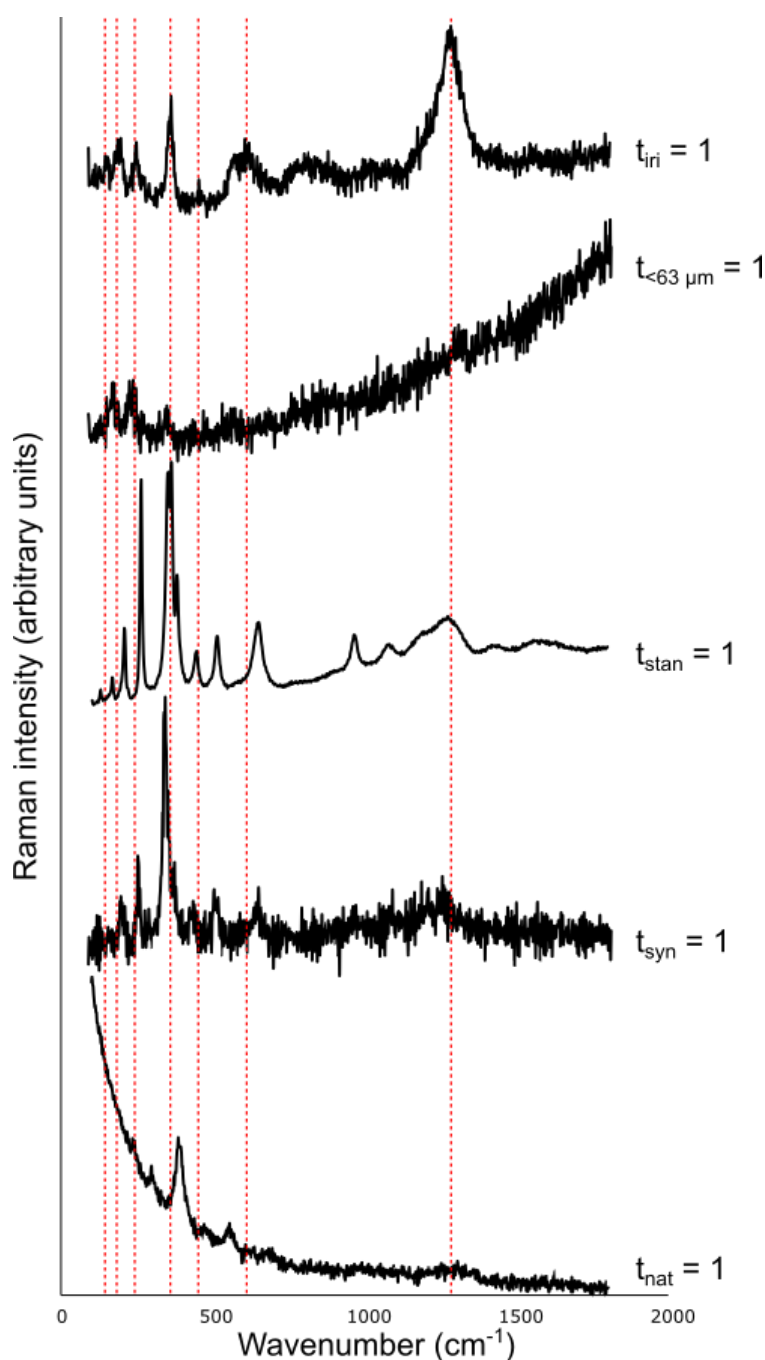


Figure 4.3 - 532 nm Raman spectra for a variety of goethite samples. *iri* - iridescent, *<63 μm* - natural sample with a grain size below $63\ \mu\text{m}$, *stan* - standard hand specimen, *syn* - synthetic powder, *nat* - natural hand specimen. Haematite peaks at $233, 293, 408, 498, 660,$ and $1317\ \text{cm}^{-1}$ are indicated with red dotted lines. *t* denotes spectrum collection order.

785 nm Raman Spectroscopy

785 nm Raman Spectroscopy was carried out on two different grain sizes $>500\text{ }\mu\text{m}$ ($t_{>500\text{ }\mu\text{m}}$) and $<63\text{ }\mu\text{m}$ ($t_{<63\text{ }\mu\text{m}}$) (Figure 4.4). Analysis of the $<63\text{ }\mu\text{m}$ grains shows the appearance of haematite within the first measurement.

Raman analysis of the $>500\text{ }\mu\text{m}$ grains shows goethite peaks which get more intense with more scans. Whilst intensity of the goethite peaks occurs, haematite peaks at 223 and 610 cm^{-1} appear at $t_{>500\text{ }\mu\text{m}} = 5$, suggesting dehydration occurring over time.

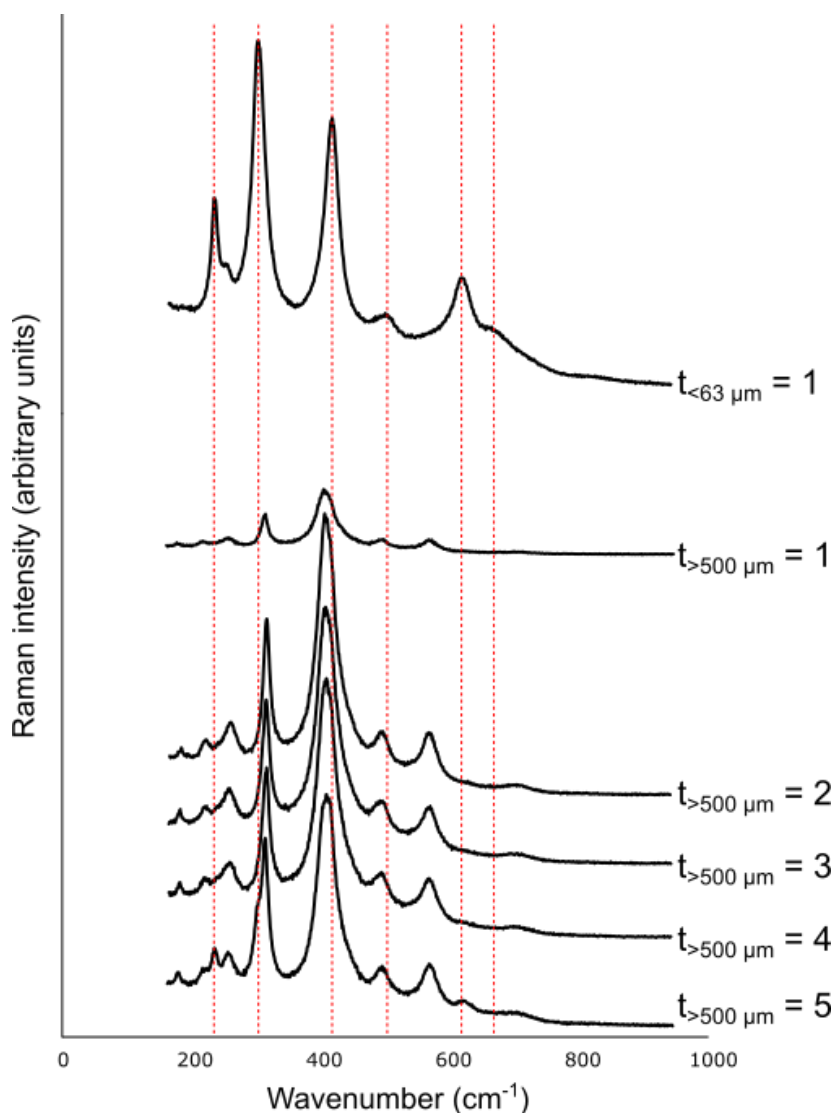


Figure 4.4 - 785 nm Raman spectra for a variety of goethite samples. $63\text{ }\mu\text{m}$ – natural sample with a grainsize below $63\text{ }\mu\text{m}$, *stan* – standard hand specimen, *syn* – synthetic powder, *nat* – natural hand specimen. Haematite peaks at 219, 237, 285, 400, 483, and 598 cm^{-1} are indicated with dotted red lines. *t* denotes spectrum collection order.

4.5.5. Haematite

785 nm Raman spectroscopy of haematite identified peaks at 225, 248, 293, 409, 495, 614 cm^{-1} all of which are assigned to haematite (Figure 4.5). 532 nm Raman spectroscopy of haematite resulted in a noisy spectrum with no identifiable peaks and is not included here.

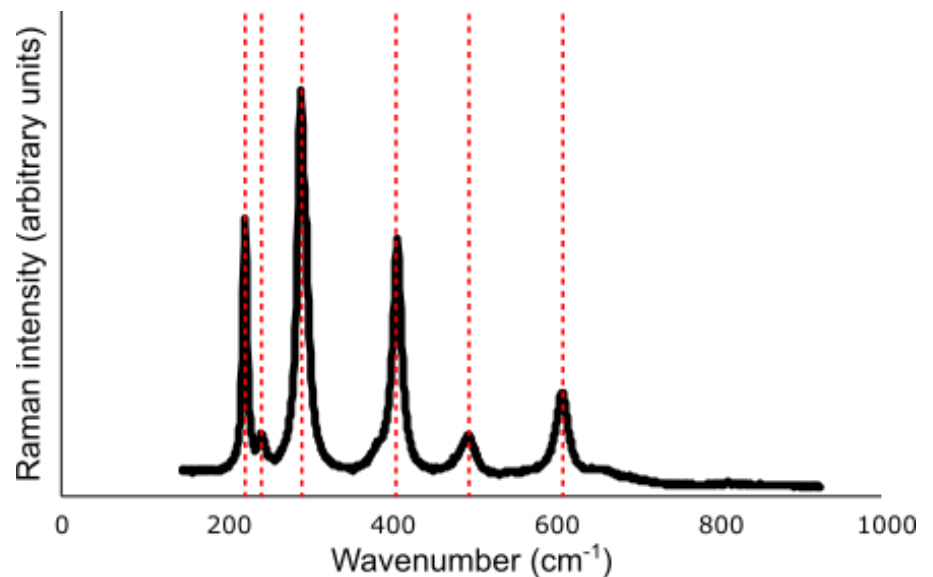


Figure 4.5 - 785 nm Raman spectra of the standard hand specimen sample of haematite

4.6 Discussion

Raman spectroscopy is a powerful tool for identifying both mineralogy and organic molecules. However, in this study we see a key downfall when Raman spectroscopy is used on iron-rich samples such as iron oxides. Many of the resulting spectra in this study were very noisy due to fluorescence from the iron oxides, which is a known problem

(Hanesch, 2009). This fluorescence is particularly bad with spectra from the shorter green (532 nm) wavelength over the longer red (785 nm) wavelength.

The rate of this laser-induced dehydration is a cause for concern. In our dataset, haematite signatures were detected in as few as the first four or five spectra collected (Figure 4.1; Figure 4.2; Figure 4.4). This is important because rover-based Raman spectrometers on Mars typically acquire between 100 and 2,000 spectra per point (Bhartia et al., 2021; Corpolongo et al., 2023; Rull et al., 2017; Wiens et al., 2021). Under these conditions, any hydrated iron oxide originally present—other than haematite—is likely to be transformed and thus absent from the final averaged spectrum transmitted to Earth. This has serious implications for the geological interpretation of Martian samples. Haematite is a dehydrated phase, and its detection over aqueous iron oxides could incorrectly suggest a drier or more oxidizing past environment, potentially skewing our understanding of past water activity and the planet's habitability.

Minerals such as magnetite and haematite are darker and strongly absorbing, creating difficulty with identification using the green 532 nm Raman spectrometer, often producing spectra full of fluorescence. To overcome this fluorescence, longer acquisition times are required, which here are observed to cause dehydration of the sample.

Using a longer wavelength laser of 785 nm over the 532 nm, shows less noisy spectra for goethite at grainsizes less than 63 μm , however both caused dehydration to haematite rapidly (Figure 4.3; Figure 4.4). Analysis of grain sizes greater than 500 μm with the 785 nm wavelength laser allows for the identification of goethite, however transformation of haematite begins to occur with the occurrence of peaks at 223 and 610 cm^{-1} over time (Figure 4.4; Table 4.2). Larger grainsizes likely allow for the dissipation of energy input from the laser, preventing dehydration for a short period of time. Rapid transformation associated with smaller grainsizes is problematic for the identification of npOx. Trying to identify npOx with Raman spectroscopy runs the risk of dehydration and potential destruction of any bound organic carbon, thus making identification of past life on Mars extremely difficult.

For the Exomars Rover, *Rosalind Franklin*, this causes extra concern. The RLS instrument onboard the rover will be used to analyse the target sample prior to the Mars Organic Molecule Analyser (MOMA) (Goesmann et al., 2017). If the Raman laser causes degradation or volatilisation of organic molecules, the MOMA instrument could yield

falsely negative results. In this scenario, genuine evidence of ancient Martian life could be lost.

Given these risks, further work is needed to:

- Quantify the rate of laser-induced dehydration for various iron oxides under different experimental conditions.
- Determine how grain size influences the rate of dehydration
- Assess how dehydration of npOx potentially affects the survival of organic molecules
- Identify the optimal laser wavelength and power settings for minimising fluorescence and sample alteration.
- Investigate how mixed-phase assemblages of iron oxides alter Raman spectral features and transformation pathways.

Addressing these points will be essential for designing observation strategies that preserve the mineralogical and organic integrity of samples on Mars, ensuring accurate interpretation of the planet's geological history and its potential to have supported life.

It is important to note that the Raman spectrometers aboard NASA's Mars 2020 Perseverance rover are optimised to detect Raman signals at relatively high wavenumbers. While this higher wavenumber range is advantageous for detecting the vibrational modes of many organic molecules, it significantly limits the ability to identify several important iron oxide phases. Minerals such as akaganeite, goethite, lepidocrocite, and schwertmannite have their most diagnostic Raman peaks below 535 cm^{-1} (Table 4.2), placing them outside the detection range of SuperCam. The SHERLOC instrument is even more restrictive, with a lower wavenumber cut-off of 800 cm^{-1} . As a result, among the most common iron oxides, haematite is the only phase that can be reliably detected by SHERLOC (Table 4.2). This instrumental limitation introduces an additional source of uncertainty into Mars 2020 mineralogical datasets: if haematite is present, there is no way to determine whether it represents a primary mineral phase or a dehydration product formed from more hydrated iron oxides during the planet's geological history—or even during laser analysis itself.

4.7 Conclusions

Raman spectroscopy is widely recognised as a powerful analytical tool for the simultaneous identification of minerals and organic compounds. Its portability, minimal

sample preparation requirements, and ability to produce rapid in-situ measurements make it particularly well-suited for planetary exploration. However, the technique faces significant challenges when applied to iron oxide-rich environments such as the Martian surface.

Iron oxides are a major component of Martian geology and, while mineralogically informative, they present two major complications for Raman spectroscopy: (1) strong fluorescence backgrounds that obscure spectral features, and (2) susceptibility to laser-induced transformation. Our results confirm that dehydration of hydrated iron oxides to haematite is a common and rapid process during Raman analysis, particularly for fine-grained materials. This transformation alters the mineralogical record during measurement, potentially leading to systematic misidentification or underrepresentation of certain phases in rover datasets.

We found that dehydration occurs more slowly in larger-grained samples and when using a longer wavelength excitation source (785 nm compared with 532 nm). Nevertheless, these conditions only delay transformation rather than prevent it, and even coarse-grained materials ultimately show evidence of phase change with prolonged laser exposure. For nanophase iron oxides (npOx), identification is especially challenging: their high surface area and low thermal inertia make them extremely vulnerable to rapid transformation. This poses an additional risk for astrobiology because npOx can bind organic carbon, and its alteration during Raman analysis could destroy organic signatures, eliminating vital evidence of past life.

The design of the Raman spectrometers on the Mars 2020 Perseverance rover introduces an additional limitation. SuperCam cannot detect key iron oxide phases such as akaganeite, goethite, lepidocrocite, and schwertmannite, as their diagnostic peaks lie below its lower wavenumber limit of 535 cm^{-1} . SHERLOC is even more restrictive, with a cut-off of 800 cm^{-1} , meaning that among the most common iron oxides, only haematite is detectable. This restriction makes it impossible to determine whether haematite detected on Mars is a primary mineral or a dehydration product, adding further uncertainty to interpretations of past Martian environments.

The implications for current and future Mars missions are substantial. Instruments such as SuperCam and SHERLOC on NASA's Perseverance rover are highly capable but, given their autonomous operation and large number of spectra averaged per target, they are prone to reporting only the dehydrated phase (haematite) even if other iron oxides were

initially present. The under-identification or misidentification of iron oxides is already evident in the published literature from Perseverance's Raman measurements (Corpolongo et al., 2023). This mineralogical bias risks distorting interpretations of past environmental conditions, particularly regarding the role of water and redox chemistry in Martian history.

To achieve a more complete and accurate understanding of Martian mineralogy, sample return remains essential. Laboratory-based analysis on Earth would allow the use of variable laser wavelengths, power settings, and complementary techniques that avoid or minimise in-situ alteration. These approaches would make it possible to confirm or refine rover-based identifications, detect minerals currently obscured by spectral limitations, and preserve any fragile organic signals for detailed astrobiological study.

In summary, while Raman spectroscopy remains a cornerstone technique for planetary mineralogy, its limitations in iron oxide-rich contexts must be carefully considered in both instrument design and data interpretation. Addressing these challenges—through further laboratory experimentation, targeted instrument calibration, and eventual sample return—will be critical for maximising the scientific return of Mars exploration missions.

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5. Analysis of Martian Analogues

5.1. Introduction

Exploration of the Martian surface by landers and rovers has been an endeavour that has been carried out by various space agencies. The first close-up images of Mars were captured by NASA's Mariner 4 in 1965, revealing a heavily cratered and barren surface. Following this, NASA were the first to successfully land on the Martian surface with the Viking 1 lander mission in 1975. Since then, several landers and rovers have landed on the Martian surface, gaining a more detailed understanding of Mars' geology, climate and potential for past or present life. Presently, two rovers are operating on the Martian surface: NASA's Mars Science Laboratory (MSL), Curiosity, and the Mars 2020 Rover, Perseverance.

Each rover carries a distinct suite of scientific instruments tailored to its mission objectives. For example, the Mars Exploration Rovers (*Spirit* and *Opportunity*) had identical payloads, while later missions incorporated more advanced and varied tools such as X-ray diffraction, Raman spectroscopy and advanced imaging systems. Each rover landed in a geologically unique areas of Mars which have undergone different processes such as volcanism, sedimentation or aqueous alteration. This presents problems when comparing data sets from the different missions as differences in measurements may arise from tools used, nature of the landing site, or both (Chapter 3).

To address these challenges, researchers turn to Martian analogue sites on Earth. Analogue sites are regions on Earth that resemble physical, chemical or geological processes on Mars. Analysing the same samples with instruments onboard the Mars rovers improves the reliability of interpretations made from rover data. This approach is important in the search for past habitability and identification of possible biosignatures.

Mars' geological history is marked by episodes of surface water, volcanic activity and a changing atmospheric composition which all have implications for preservation or destruction of potential evidence of life. Reactive iron minerals, for instance, can either protect organics by binding them or accelerate their breakdown through oxidation. Understanding these processes in Earth analogues helps in evaluating the preservation potential of Martian environments.

The study of analogues also directly informs mission planning. ESA's upcoming ExoMars rover, *Rosalind Franklin*, will use instruments such as the Raman Laser Spectrometer to investigate mineralogy and search for organic compounds. Insights from analogue research are vital for interpreting these measurements and anticipating potential complications, such as fluorescence from iron oxides masking organic signals or the transformation of iron oxides causing the destruction of organic matter (Chapter 4). Likewise, findings from analogue studies will be essential when samples are eventually returned to Earth through NASA's Mars Sample Return programme.

In this chapter, I present an analysis of several terrestrial analogue sites, ranging from marine sediment cores to ancient mudstones, chosen for their relevance to Martian surface environments. The chapter outlines the methods employed—including Mössbauer spectroscopy, X-ray diffraction, Raman spectroscopy, and sequential extractions—followed by detailed results for each site. The discussion compares the capabilities and limitations of each technique in detecting reactive iron species, associated organics and considers the implications for interpreting data from current and future Mars missions.

5.2. Methods

For methodology of Mössbauer spectroscopy, XRD, Raman spectroscopy, sequential extractions, and ICP-OES and C/N analysis, see Chapter 2.

5.2.1. Identification of reactive iron species

Reactive iron species are identified here with Mössbauer spectroscopy as nanophase iron oxides (npOx). Identification is based on several factors: similar parameters with npOx or the Fe3D3 doublet observed on Mars (Morris 2008, 2006a, 2006b) and the occurrence of superparamagnetism. Superparamagnetism is observed by the magnetic alignment of nanoparticulate iron oxides below the Curie or Néel temperatures (the temperatures at which a material loses its ordered magnetic state). For example, goethite has a Néel temperature of 400 K (Yoshida and Langouche, 2013), meaning superparamagnetism will only be observed in temperatures below this. Temperature dependent Mössbauer spectroscopy allows for this to be clearly seen within the resulting Mössbauer spectra.

Reactive iron species are X-ray amorphous, meaning they are difficult to observe with XRD. The CheMin instrument onboard the MSL rover observed X-ray amorphous material as wide peaks at $\sim 25^\circ 2\theta$. The Alpha Particle X-ray Spectrometer (APXS) results were used to fully quantify the amount of iron-rich X-ray amorphous (AmoFe) material within the samples measured by the MSL rover (Rampe et al., 2017). This material is difficult to quantify without further calculations, making identification of reactive iron with CheMin difficult.

It is currently unclear whether reactive iron species can be identified by Raman spectroscopy. The identification of iron oxides with Raman spectroscopy is previously in Chapter 4.

5.3. Materials

Mars analogues are samples from Earth that can be compared to the Martian surface through various properties or depositional environments, for example, Rio Tinto, Spain is an analogue for past Mars (Amils et al., 2007; Fernández-Remolar et al., 2005; Preston and Dartnell, 2014), whilst the Atacama Desert, Chile is an analogue for present Mars (Preston and Dartnell, 2014). Following the classification described in Preston and Dartnell, (2014) and Soare *et al.*, (2001), the sites selected for this study range in how applicable they are to Mars.

‘Analogues of the first order’ are samples that are from area that have been directly observed on the surface of Mars, for example volcanic rocks or dust devils (Preston and Dartnell, 2014; Soare et al., 2001). ‘Analogues of the second order’ are based on indirect evidence, for example, there is indirect evidence of fluvial and lacustrine activity on the surface of Mars, such as the presence of goethite (a hydrated iron oxide) observed by both Mars Exploration Rovers (Morris et al., 2006a, 2006b) or stratigraphic columns analysed by the MSL rover (Rampe et al., 2017). ‘Analogues of the third order’ are defined as not having direct or indirect evidence. An example of this would be extremophiles. Whilst there is no evidence of life elsewhere in the solar system, it can be inferred that certain forms of life such as iron reducing microorganisms could survive on the Martian surface (Nixon et al., 2012, 2017, 2022). However, classification using this system can be complex, with different factors needing to be considered, for example a depositional environment can be classified as a first order analogue but features within the sample on a smaller scale can be classified as second order.

Samples used within this chapter have characteristics that reflect potential past Martian environments, making them valuable samples to analyse.

5.3.1. North Sea (UK)

The Scanner

Pockmark is an active pockmark in the North Sea. Pockmarks are circular depressions in the ocean floor and indicate fluid flow from a methane rich subsurface (Böttner et al., 2019). Whilst not formally identified on the Martian surface, pockmarks are morphologically



Figure 5.1 - Location map of the Scanner Pockmark

similar to small craters, so could be misidentified (Allen et al., 2013; Komatsu et al., 2011)

The occurrence of pockmarks on Mars could explain the controversial methane detected by various authors (Komatsu et al., 2011).

The sediment core used in this study was collected by Allan Audsley (University of Stirling, UK) in 2019 with a gravity corer at the Southern Scotia pockmark within the Scanner Pockmark Special Area of Conservation (SAC) in the North Sea, ~185 km off the northeast coast of Scotland (Figure 5.1). Throughout the core, black, magnetic solid nodules were observed. These nodules oxidised when exposed to air, losing their magnetism. Both forms of nodules were analysed, along with surrounding clay and clay on an iron change boundary (Figure 5.2; Table 5.1). All samples were ground manually and left to air dry prior to analysis.

Samples from this region are classified as second order analogues due to the occurrence of pockmarks on the surface of Mars being inferred with no direct evidence. However, the nodules within the core can be classified as first order analogues due to similar nodules

(nicknamed ‘Blueberries’) observed by the Mars Exploration Rovers on the Martian surface (Morris et al., 2006a, 2006b).

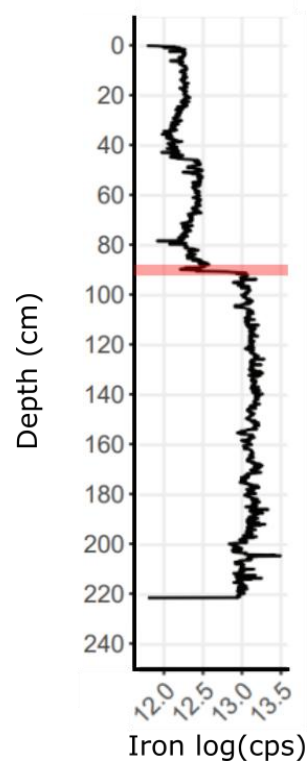


Figure 5.2 - Itrax-XRF graph showing iron count with depth. Change in iron is highlighted in red (figure credit to Allan Audsley, University of Stirling)

Table 5.1 - Table showing samples analysed from the North Seas pockmark core and their depth

Sample	Depth (m)	Description
GC027_01	1.64	Grey clay adjacent to a cluster of the hard nodules
GC027_02	1.61	Grey clay above a cluster of the hard nodules
GC027_03	1.67	Grey clay below a cluster of the hard nodules
GC027_05	0.90	Grey clay near the change in iron seen in Itrax-XRF plot (Figure 5.2)
GC027_06	0.80	Grey clay above the change in iron as seen in Itrax-XRF plot (Figure 5.2)
GC027_07	~1.64	Brown, non-magnetic hard nodules throughout core
GC027_0B	~1.64	Black, magnetic hard nodules throughout core

5.3.2. Danube Delta/Black Sea (Romania)

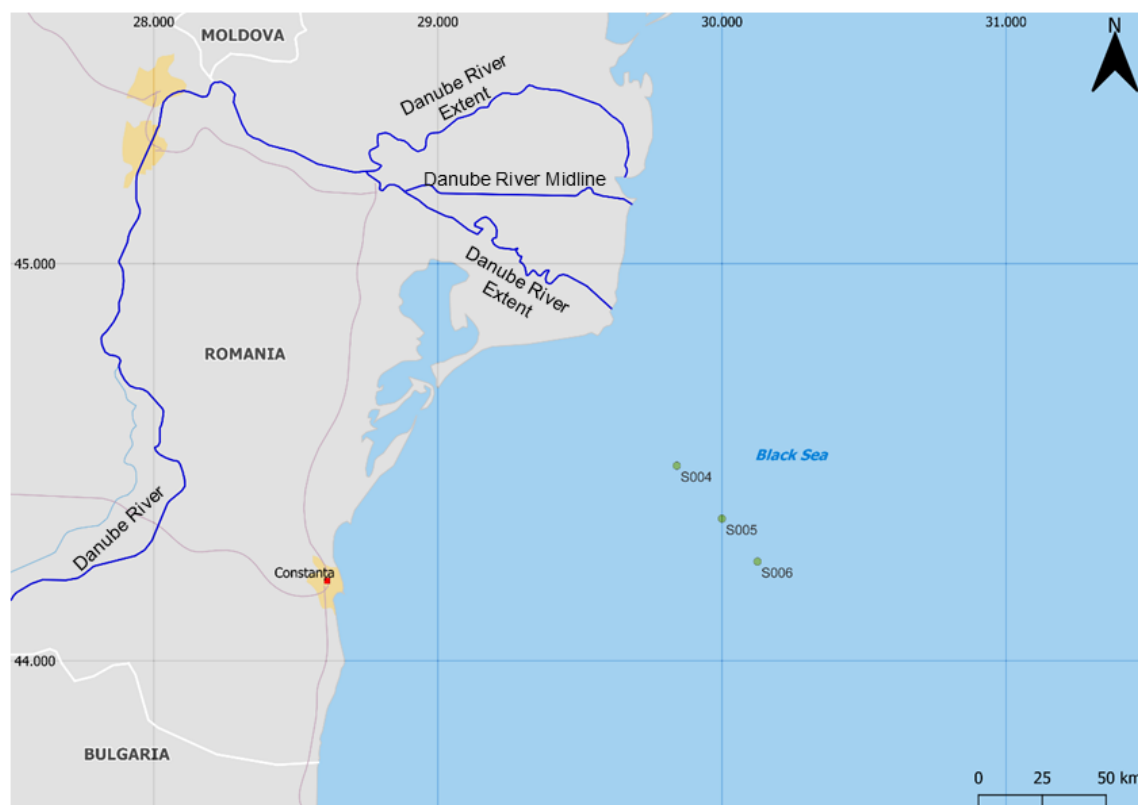


Figure 5.3 - Location map of the cores collected from the Danube Delta/Black Sea

The Danube River forms a natural border between Romania and Ukraine before flowing into the Black Sea. The change from a fluvial environment to a lower velocity fluid environment of the Black Sea causes sediment in suspension to be deposited, forming a delta. The Black Sea is known for its euxinic conditions (being both anoxic and sulfidic) (Raiswell and Canfield, 2012), making it a good comparison to Mars (Liu et al., 2021), along with the delta environment making it comparable to the Mars 2020 rover, *Perseverance*, landing site (Stack et al., 2020). Samples were collected by Adriana Constantinescu (GeoEcoMar, Bucharest, Romania) as part of the project ReCoReD, funded through EuroFleets 2, on board RV Mare Nigrum, belonging to NIRD GeoEcoMar in 2016.

Cores used came from the prodelta section of the Danube delta. A prodelta is a region of passive sedimentation from suspension that is only disturbed by gravity sliding or mass flow deposition (Reading, 1996). Cores S004, S005 and S006 were gathered with a multi-corer offshore from Romania (Figure 5.3) Samples used from each core came from the top cm and the bottom cm (depending on the length of the core) (Table 5.2). Frozen samples for Mössbauer spectroscopy analysis were placed into the acrylic glass holder with

minimal defrosting and then measured at 4 and 77 K before room temperature measurements to limit exposure to oxygen and prevent defrosting causing transformation of potential unstable iron sulphide minerals within the samples. For XRD, Raman spectroscopy, and sequential extractions, sediment was freeze-dried and ground to a fine powder prior to analysis. Oxidation of iron sulphides may have occurred during this treatment.

Samples from the Black Sea are classified as second order analogues due to the current lack of water on the surface of Mars, however it can be inferred that there was deltas on the Mars' surface (Stack et al., 2020). This is doubled with the inferred euxinic and sulfidic nature of Mars in the past (Liu et al., 2021).

Table 5.2 -Table showing samples analysed from the Black Sea core samples

Core ID	Type	Area	Length (cm)	Water depth (m)	Core depths sampled (cm)
MN148 - S004	MUC*	Prodelta offshore	34	61.7	01, 33
MN148 - S005	MUC	Prodelta offshore	29	68.2	01, 29
MN148 - S006	MUC	Prodelta offshore	32	79.6	01, 30

5.3.3. Whitby (UK)

The Alum Shale member is a part of the Jurassic aged Whitby mudstone formation that outcrops along the North Yorkshire coast, UK. Samples were collected at Whitby in Spring 2021 at 3 different points along the coast (Figure 5.4) from debris at the cliff base (direct sampling of the cliff is prohibited due to site of special scientific interest status).



Figure 5.4 - Location map of samples collected along the Whitby coast

Collected samples are various shades of gray in colour with a fine grainsize. The Alum Shale is of interest for this study due to its depositional environment being oxygen-poor (reduced) (Raiswell and Canfield, 2012), similar to the reduced depositional environments observed on Mars (Liu et al., 2021). It has also been noted to contain reactive iron species (Raiswell and Canfield, 2012).

Samples were collected with the assistance of Poppy Bonsall. The rocks collected varied in colour, with AlSh3 being the darkest in colour, AlSh2 being the lightest and AlSh1 being in between the 2. All samples were ground manually with a pestle and mortar into a fine powder prior to analysis.

Samples from the Alum shale member along the Whitby coastline are classified as second order analogues due to the inferred reduced depositional environments on Mars (Liu et al., 2021).

5.3.4. Coulter Quarry (UK)

The Marchburn Formation in the Northern Belt of the Southern Uplands of Scotland is of Ordovician age (Barron et al., 2004). Within this formation are lenticular beds of



Figure 5.5 - Location map of the Coulter Quarry

microconglomerates locally known as “Haggis Rock” due to its appearance looking similar to that of the inside of a Haggis (Barron et al., 2004; Ritchie and Eckford, 1936). The Haggis Rock is composed of clasts of red, green-grey, and black chert and mudstone fragments along with basalt, quartz, felsic igneous and high-grade metasedimentary clasts set in a green-grey matrix (Barron et al., 2004; Ritchie and Eckford, 1936). The presence of detrital clinopyroxene in the matrix suggests a basic igneous rock source with a short transport distance (Barron et al., 2004). The Haggis Rock is comparable to Mars as the conglomeritic rocks encountered on Mars are from an igneous source rock, not a sedimentary source like what is most seen on Earth (McLennan et al., 2019). Samples of the Haggis Rock samples were collected during a fieldtrip with the ESA ExoMars Raman Laser Spectrometer team early in 2022. A sample of the Haggis rock was collected from Coulter Quarry (55.583422, -3.542869), ~80 km SE of Glasgow, Scotland, UK (Figure 5.5). A portion of the rock was crushed and ground into a fine powder for analysis.

The Coulter Quarry samples can be classified as a first order analogue as there is direct evidence of basaltic rich sedimentary rocks observed by various rovers on the Mars' surface (McLennan et al., 2019)

5.4. Results

5.4.1. Mössbauer Spectroscopy

Mössbauer spectroscopy identifies iron mineral phases and oxidation states within samples. These features are identified by singlets (features with 1 peak), doublets (features with 2 peaks), and sextets (features with 6 peaks). Parameters of spectral peaks are given as functions of isomer shift of doublets and sextets (δ), quadrupole split for doublets (ΔE_Q), quadrupole shift for sextets (ϵ), magnetic hyperfine field of sextets (B_{hf}) and line width (Γ). The relative areas of the subspectra are proportional to the percentage of the identified mineral out of the total iron in the sample.

North Sea Pockmark (UK)

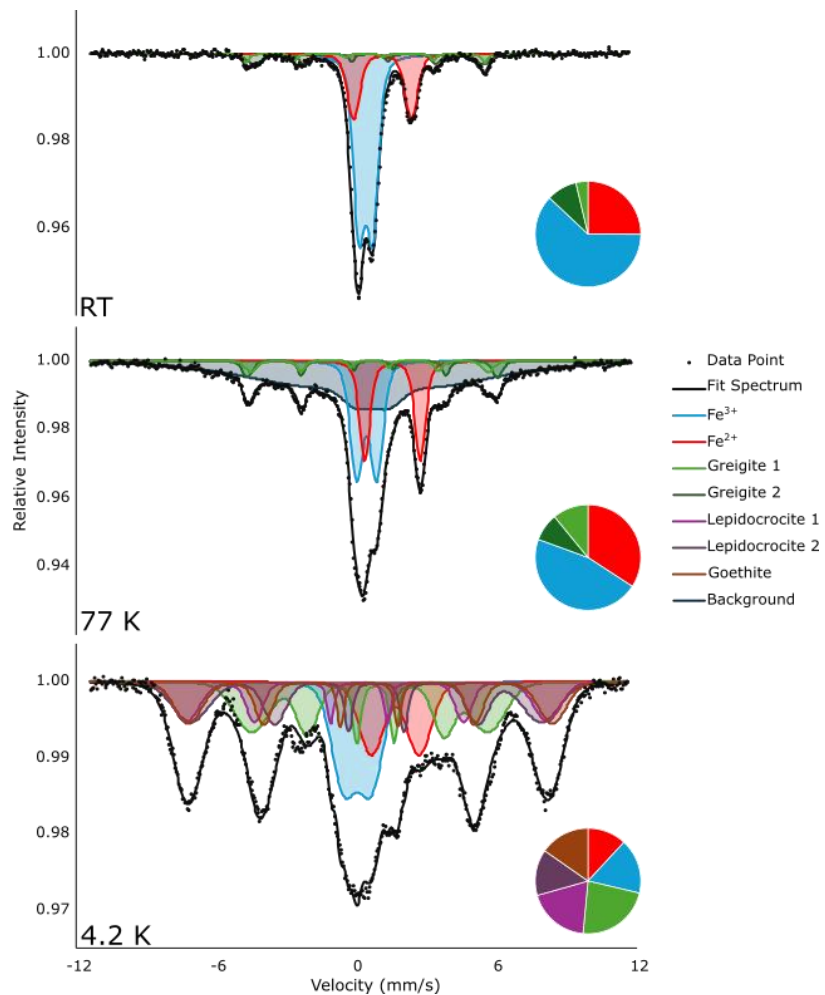


Figure 5.6 - Temperature dependent Mössbauer spectra of GC027 01 with pie charts showing percentage of minerals identified

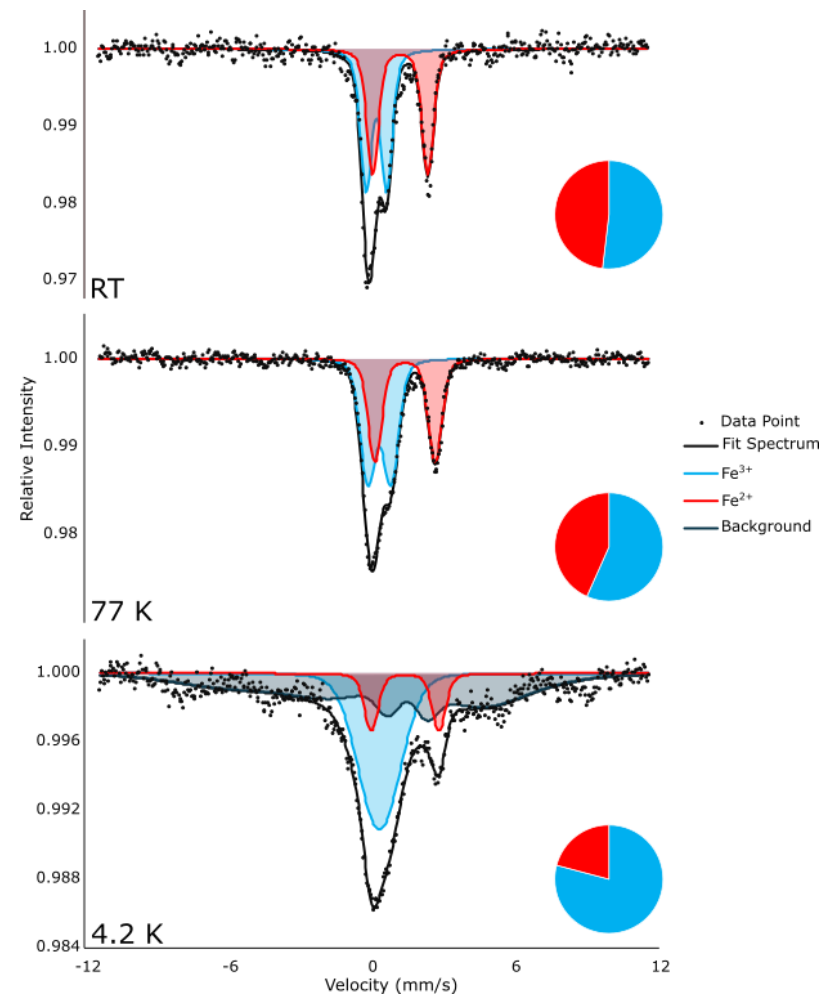


Figure 5.7 - Temperature dependent Mössbauer spectra of GC027 02 with pie charts showing percentage of minerals identified

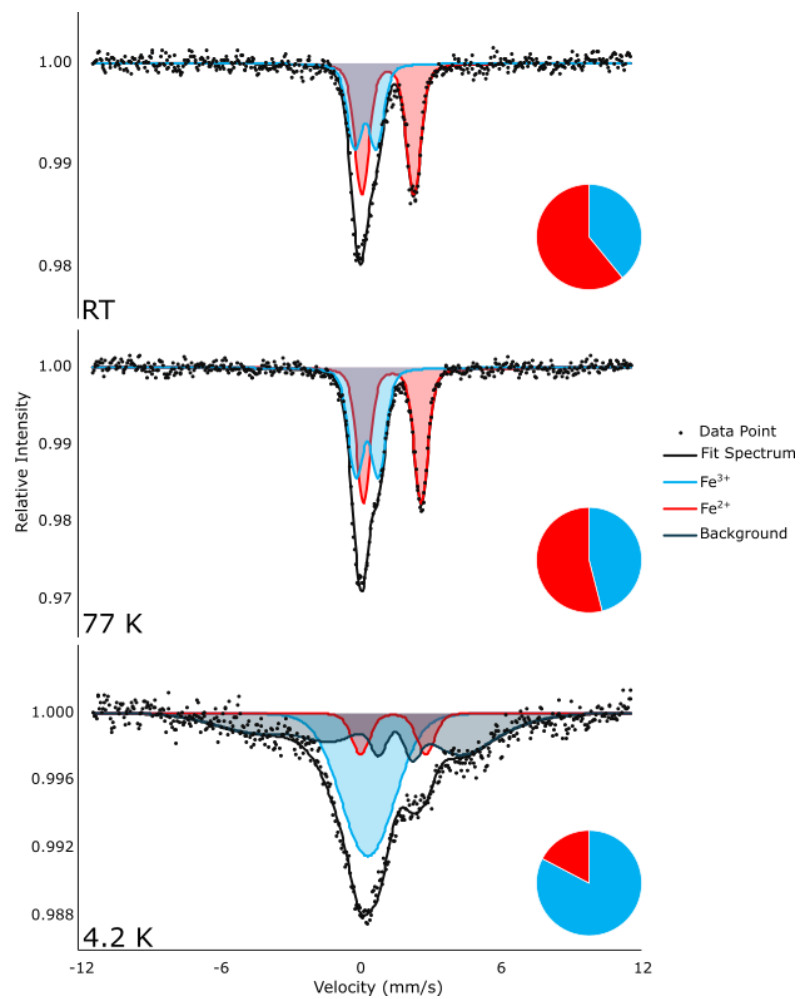


Figure 5.8 - Temperature dependent Mössbauer spectra of GC027 03 with pie charts showing percentage of minerals identified

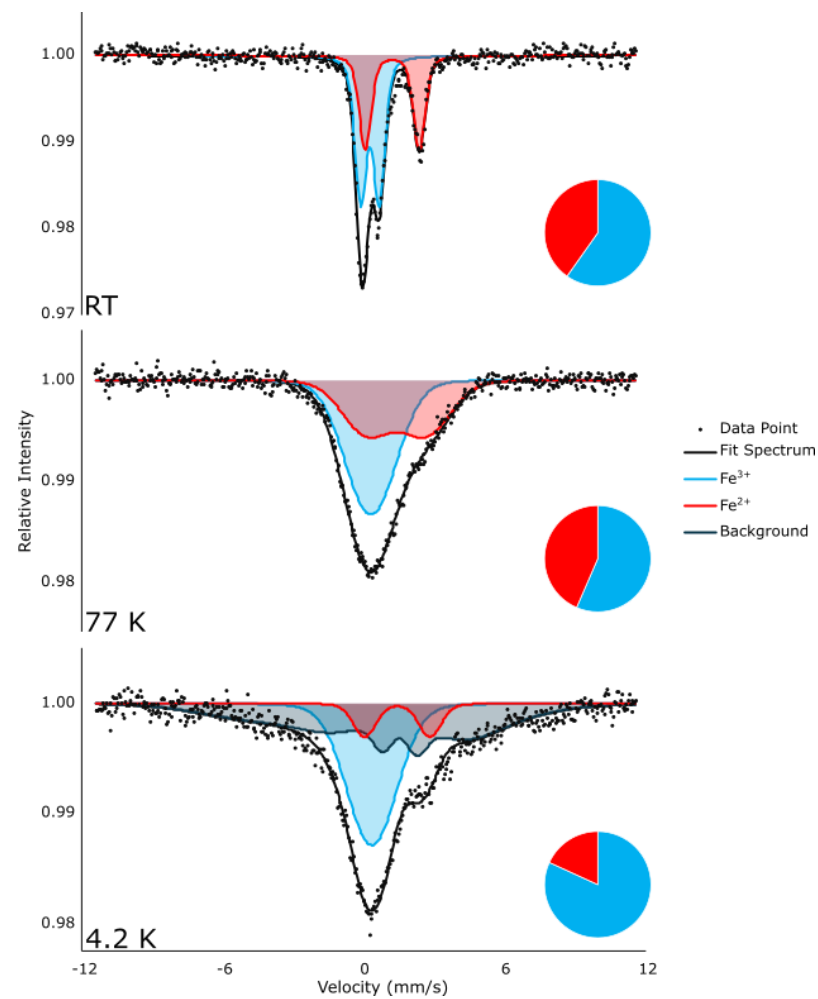


Figure 5.9 - Temperature dependent Mössbauer spectra of GC027 05 with pie charts showing percentage of minerals identified

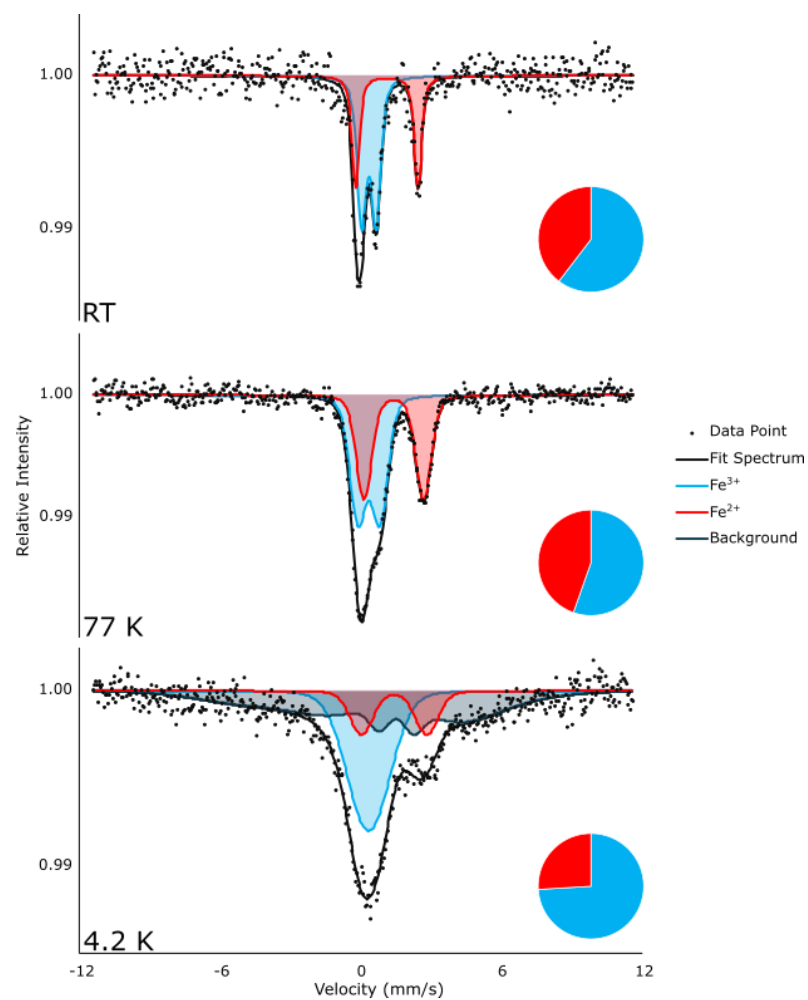


Figure 5.10 - Temperature dependent Mössbauer spectra of GC027 06 with pie charts showing percentage of minerals identified

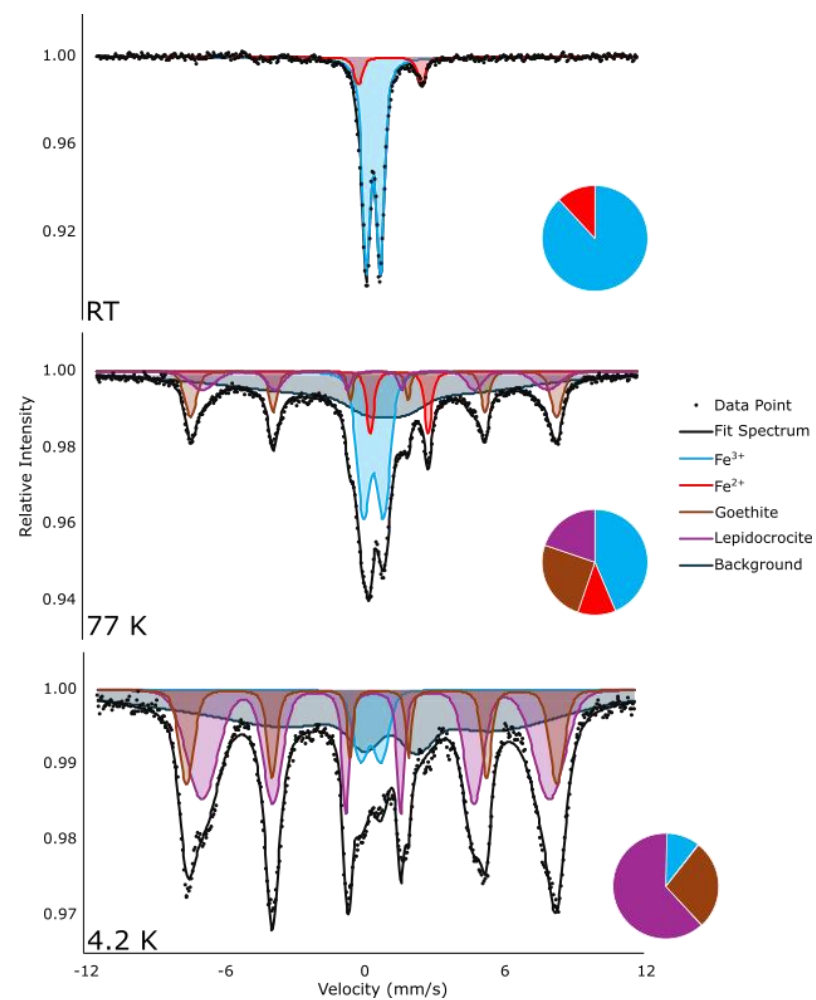


Figure 5.11 - Temperature dependent Mössbauer spectra of GC027 07 with pie charts showing percentage of minerals identified

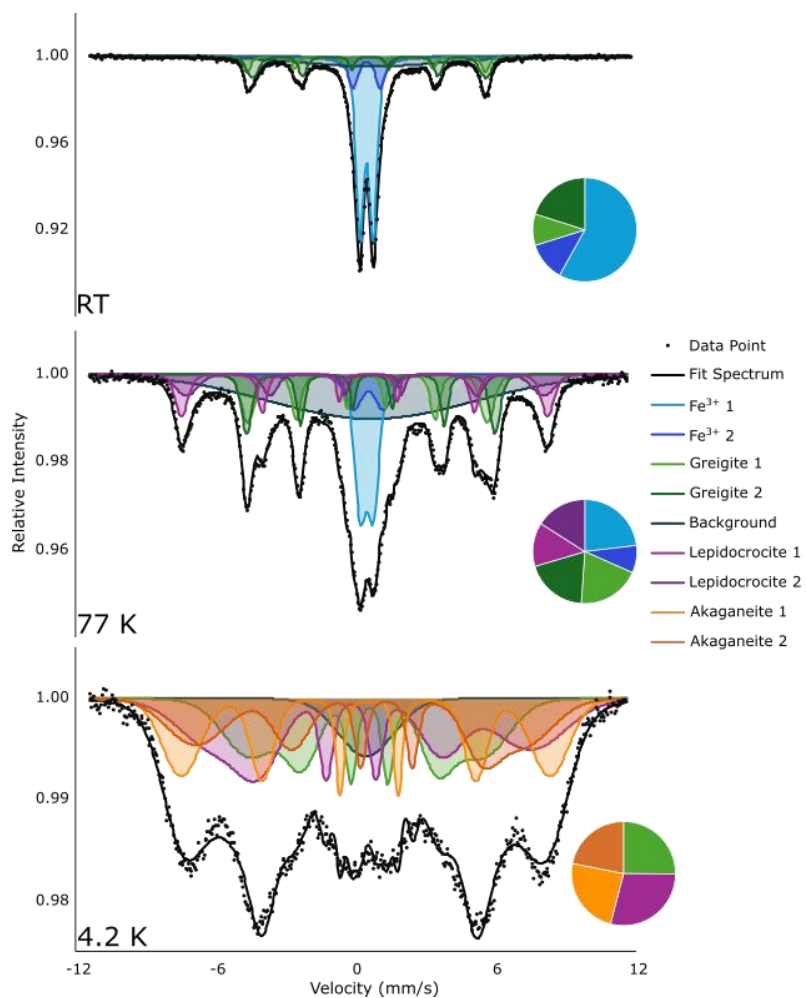


Figure 5.12 - Temperature dependent Mössbauer spectra of GC027 B with pie charts showing percentage of minerals identified

Table 5.3 - Mössbauer spectra parameters of GC027 01

Mineral Phase	δ (mm/s)	ΔE_Q or ε (mm/s)	B_{hf} (T)	Γ (mm/s or T)	Peak Area (%)	Mineral total (%)	Temperature
Fe3+ (npOx)	0.37	0.59	-	0.38	62	62.0	RT
Fe2+	1.08	2.47	-	0.42	25.1	25.1	
Greigite 1	0.51	-0.02	30.3	1.62	9.3	13.0	
Greigite 2	0.33	0.02	31.6	0.25	3.7		
Fe3+ (npOx)	0.35	0.89	-	0.44	22.9	22.9	77 K
Fe2+	1.44	2.36	-	0.34	16.9	16.9	
Greigite 1	0.47	0.00	31.3	1.21	4.2	9.6	
Greigite 2	0.62	-0.03	33.0	0.96	5.4		
Background	0.54	-0.05	25.8	21.54	50.6	50.6	
Fe3+	0.03	1.17	-	0.93	16.8	16.8	4.2 K
Fe2+	1.64	2.04	-	0.95	11.9	11.9	
Greigite	0.68	-0.12	31.3	4.35	22.8	22.8	
Lepidocrocite 1	0.61	-0.22	46.4	4.52	19.1	33.2	
Lepidocrocite 2	0.26	0.16	47.8	3.24	14.1		
Goethite	0.55	0.02	48.3	3.36	15.3	15.3	

Table 5.4 - Mössbauer spectra parameters of GC027 02

Mineral Phase	δ (mm/s)	ΔE_Q or ε (mm/s)	$B_{hf}(T)$	Γ (mm/s or T)	Peak Area (%)	Mineral total (%)	Temperature
Fe3+	0.24	0.86	-	0.37	51.9	51.9	RT
Fe2+	1.24	2.31	-	0.38	48.1	48.1	
Fe3+	0.34	0.96	-	0.55	56.7	56.7	77 K
Fe2+	1.41	2.52	-	0.47	46.3	46.3	
Fe3+	0.32	0.37	-	1.63	40.6	41	4.2 K
Fe2+	1.39	2.83	-	0.47	10.7	12.4	
Background	0.66	-0.83	32.2	16.5	48.8	37.1	

Table 5.5 - Mössbauer spectra parameters of GC027 03

Mineral Phase	δ (mm/s)	ΔE_Q or ε (mm/s)	$B_{hf}(T)$	Γ (mm/s or T)	Peak Area (%)	Mineral Total (%)	Temperature
Fe3+	0.25	0.92	-	0.52	39.1	39.1	RT
Fe2+	1.21	2.21	-	0.51	60.9	60.9	
Fe3+	0.32	0.96	-	0.54	46.0	46.0	77 K
Fe2+	1.39	2.46	-	0.47	54.0	54.0	
Fe3+	0.35	0.13	-	2.18	46.8	46.8	4.2 K
Fe2+	1.43	2.78	-	0.67	9.8	9.8	
Background	0.92	-0.61	28.1	11.5	43.3	43.3	

Table 5.6 - Mössbauer spectra parameters of GC027 05

Mineral Phase	δ (mm/s)	ΔE_Q or ε (mm/s)	$B_{hf}(T)$	Γ (mm/s or T)	Peak Area (%)	Mineral Total (%)	Temperature
Fe3+	0.27	0.79	-	0.38	59.8	59.8	RT
Fe2+	1.22	2.30	-	0.40	40.2	40.2	
Fe3+	0.32	0.96	-	1.79	56.5	56.5	77 K
Fe2+	1.41	2.52	-	2.00	43.5	43.5	
Fe3+	0.35	0.13	-	2.04	42.8	42.8	4.2 K
Fe2+	1.43	2.78	-	0.86	9.5	9.5	
Background	0.92	-0.61	28.4	15.5	47.7	47.7	

Table 5.7 - Mössbauer spectra parameters of GC027 06

Mineral Phase	δ (mm/s)	ΔE_Q or ε (mm/s)	$B_{hf}(T)$	Γ (mm/s or T)	Peak Area (%)	Mineral Total (%)	Temperature
Fe3+	0.33	0.62	-	0.28	60.4	60.4	RT
Fe2+	1.10	2.65	-	0.19	39.6	39.6	
Fe3+	0.33	0.93	-	0.60	55.4	55.4	77 K
Fe2+	1.39	2.54	-	0.56	44.6	44.6	
Fe3+	0.35	0.13	-	1.72	40.8	40.8	4.2 K
Fe2+	1.43	2.78	-	0.88	14.3	14.3	
Background	0.92	-0.61	28.4	15.05	44.9	44.9	

Table 5.8 - Mössbauer spectra parameters of GC027 07

Mineral Phase	δ (mm/s)	ΔE_Q or ε (mm/s)	B_{hf} (T)	Γ (mm/s or T)	Peak Area (%)	Mineral Total (%)	Temperature
Fe3+ (npOx)	0.37	0.60	-	0.22	88.1	88.1	RT
Fe2+	1.08	2.69	-	0.23	11.9	11.9	
Fe3+ (npOx)	0.37	0.85	-	0.47	23.6	23.6	77 K
Fe2+	1.47	2.46	-	0.18	6.3	6.3	
Goethite	0.49	-0.12	48.2	1.19	13.5	13.5	
Lepidocrocite	0.43	0.01	45.5	2.96	10.7	10.7	
Background	0.41	-0.48	30.9	29.62	46.0	46.0	
Fe3+	0.30	0.89	-	0.55	6.3	6.3	4.2 K
Goethite	0.51	-0.16	49.2	1.59	16.5	16.5	
Lepidocrocite	0.46	0.05	46.1	3.75	37.3	37.3	
Background	0.63	-0.52	41.9	25.00	46.0	46.0	

Table 5.9 - Mössbauer spectra parameters of GC027 B

Mineral Phase	δ (mm/s)	ΔE_Q or ε (mm/s)	B_{hf} (T)	Γ (mm/s or T)	Peak Area (%)	Mineral Total (%)	Temperature
Fe3+ 1	0.37	0.56	-	0.21	47.1	47.1	RT
Fe3+ 2	0.37	1.15	-	0.29	9.8	9.8	
Greigite 1	0.30	0.05	31.4	0.51	7.9	24.2	
Greigite 2	0.49	-0.03	30.7	1.25	16.3		
Background	0.60	-0.01	-	5.94	18.9	18.9	
Fe3+ 1	0.46	0.57	-	0.38	14.6	14.6	77 K
Fe3+ 2	0.53	1.28	-	0.63	5.4	5.4	
Greigite 1	0.46	0.04	31.7	1.46	12.3	24.5	
Greigite 2	0.67	-0.04	32.9	1.05	12.2		
Lepidocrocite 1	0.57	-0.18	47.3	2.68	8.6	18.7	
Lepidocrocite 2	0.45	-0.08	48.5	1.35	10.1		
Background	0.69	-0.09	-	8.66	36.9	36.9	4.2 K
Greigite	0.5	-0.07	30.7	6.84	23.6	23.6	
Lepidocrocite	0.27	0.48	41.7	9.16	27.2	27.2	
Akaganeite 1	0.49	-0.07	48.9	4.73	22.6	22.6	
Akaganeite 2	0.73	-0.58	43.3	7.46	20.6	20.6	
Background	0.43	0.00	-	2.27	6.1	6.1	

GC027 01

Sample GC027 01 was obtained from clay next a cluster of solid nodules (Table 5.1). Room temperature Mössbauer spectroscopy identified greigite sextets (both tetrahedral and octahedral sites), and Fe^{2+} and Fe^{3+} doublets (Figure 5.6; Table 5.3). The Fe^{3+} doublet has similar parameters as the Fe3D3 doublet identified on Mars by the Opportunity rover (Morris et al., 2006a), classified in Chapter 3 as nanophase iron (oxyhydr)oxides (npOx). As temperatures are lowered to 77 K, a background feature appears (Figure 5.6). The relative decrease in both Fe^{2+} and Fe^{3+} percentages at 77 K (Table 5.3) suggests a portion of these phases began to magnetically align causing the appearance of the background sextet (Figure 5.6). The background sextet is not present at 4.2 K, suggesting the particles are superparamagnetic and

have magnetically aligned to form distinct sextets (Figure 5.6). The peak area decrease of the Fe^{3+} doublet with decreasing temperature and appearance of sextets confirms the presence of npOx. These sextets have been identified as lepidocrocite and goethite. Lepidocrocite is fit with 2 sextets as particle morphology has an effect on crystallinity causing differences in the observed Mössbauer subspectra (Murad and Schwertmann, 1984). The remaining Fe^{3+} doublet at 4.2 K has unusual parameters which are likely a combination of non-crystalline minerals (such as clays) overlapping and obscuring the separate peaks.

GC027 02, 03, 05

Sample GC027 02 was obtained from clay above a cluster of the solid nodules, sample GC027 03 was from clay below these nodules and GC027 05 was clay near a change in Fe amount (Table 5.1). Room temperature Mössbauer spectroscopy observed Fe^{2+} and Fe^{3+} doublets in all 3 samples (Figure 5.7-5.9; Table 5.4-5.6). The Fe^{3+} doublet parameters (Table 5.4-5.6) do not align with npOx parameters (Morris et al., 2006a, 2006b). At 77 K there is no change in observed subspectra except for parameter increase which is expected at lower temperatures (Yoshida and Langouche, 2013). At 4.2 K, a background feature appears (Figure 5.7-5.9; Table 5.4-5.6). Due to the relative reduction in Fe^{2+} peak area between the 77 and 4.2 K spectra (Figure 5.7-5.9; Table 5.4-5.6), it can be assumed that the background feature is likely due to part of the Fe^{2+} fraction weakly magnetically aligning.

GC027 06

Sample GC027 06 was obtained from clay above a change in Fe amount (Table 5.1). Room temperature Mössbauer spectroscopy observed Fe^{2+} and Fe^{3+} doublets in all 3 samples (Figure 5.10; Table 5.7). The Fe^{3+} doublet parameters (Table 5.7) do align with either Fe3D3 or npOx parameters (Morris et al., 2006a, 2006b). At 77 K there is no change in observed subspectra except for parameter increase which is expected at lower temperatures (Yoshida and Langouche, 2013). At 4.2 K, a background feature appears (Figure 5.10; Table 5.7). Due to the relative reduction in Fe^{2+} amount between the 77 and 4.2 K spectra (Figure 5.10; Table 5.7), it can be assumed that the background feature is likely due to part of the Fe^{2+} fraction to weakly magnetically align and instead associated with clay minerals, not iron oxides along with the Fe^{3+} fraction.

GC027 07

Sample GC027 07 was a collection of brown, non-magnetic, solid nodules throughout the core (Table 5.1). Room temperature Mössbauer spectroscopy showed a spectrum dominated by Fe^{3+} with minor Fe^{2+} doublets (Figure 5.11; Table 5.8). The Fe^{3+} doublet has parameters similar to FeD3 or npOx (Morris et al., 2006a, 2006b). As the temperature is decreased to 77 K, 3 sextets appear: lepidocrocite, goethite and a background phase (Figure 5.11; Table 5.8). Lepidocrocite is fit with a single sextet unlike GC027 01, suggesting a more uniform particle morphology along with a higher degree of crystallinity to appear at 77 K (Murad and Schwertmann, 1984). At 4.2 K, the Fe^{2+} doublet is no longer observed, likely obscured by the background sextet or being incorporated into the background feature due to weak magnetic alignment as described in samples GC027 02-06. At 4.2 K, lepidocrocite becomes the dominant phase. Superparamagnetic goethite is observed in the 77 and 4.2 K spectra (Figure 5.11).

GC027 B

Sample GC027 B was a collection of black, magnetic, solid nodules throughout the core (Table 5.1). Room temperature Mössbauer spectroscopy identified greigite sextets (both tetrahedral and octahedral sites), two Fe^{3+} doublets, along with a background feature (Figure 5.12; Table 5.9). These phases remain present at 77 K, with the addition of lepidocrocite as two sextets. At 4.2 K, greigite and lepidocrocite is fit with a single sextet, likely due to similar reasons as those describe in sample GC027 01. Two new sextets appear at 4.2 K and are identified as akaganeite (Table 5.9). The lack of superparamagnetism of either of the Fe^{3+} doublets suggest an absence of npOx.

Danube Delta/Black Sea (Romania)

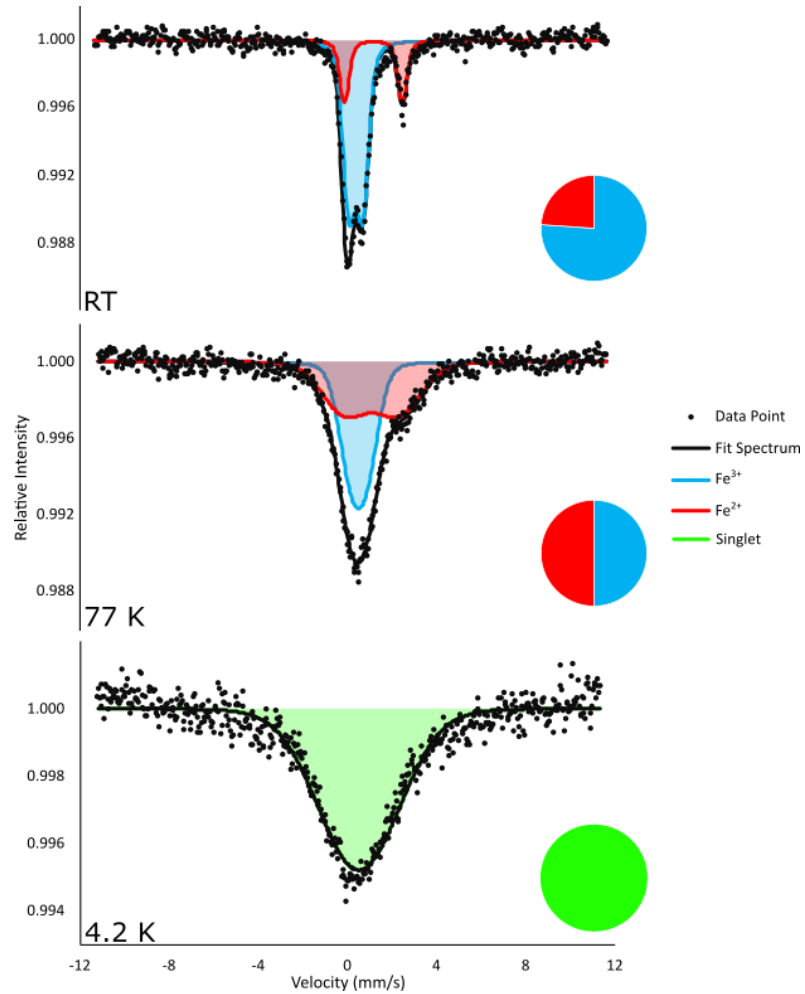


Figure 5.13 - Temperature dependent Mössbauer spectra of MN148 S004 01 with pie charts showing percentage of minerals identified

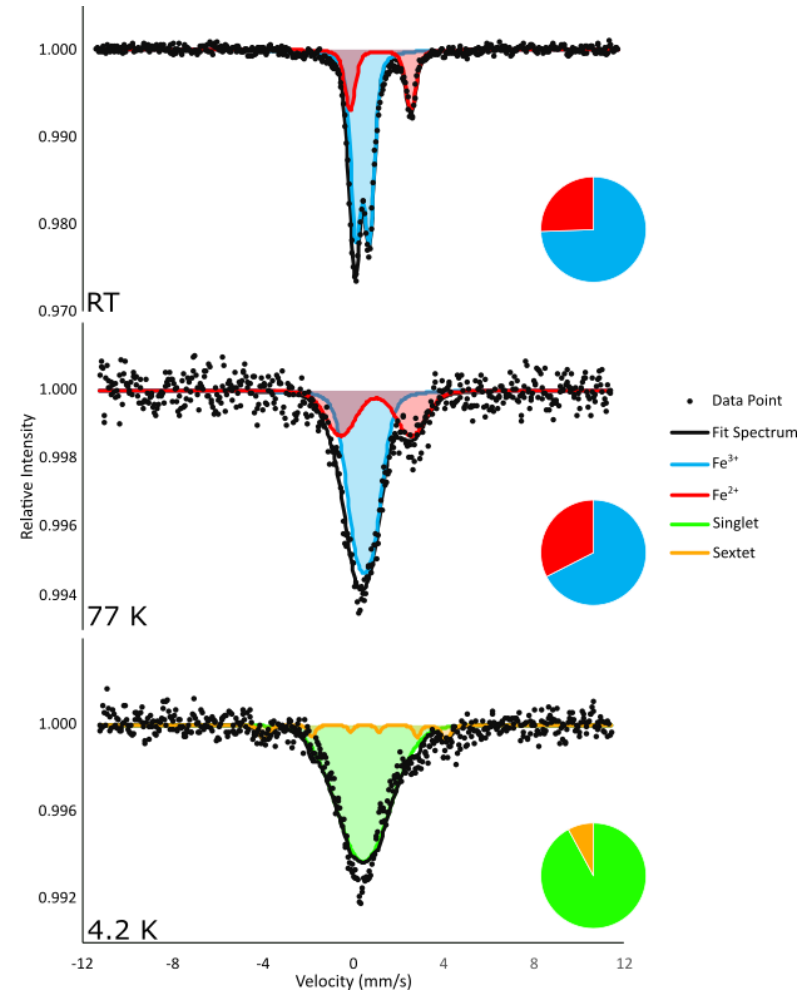


Figure 5.14 - Temperature dependent Mössbauer spectra of MN148 S004 33 with pie charts showing percentage of minerals identified

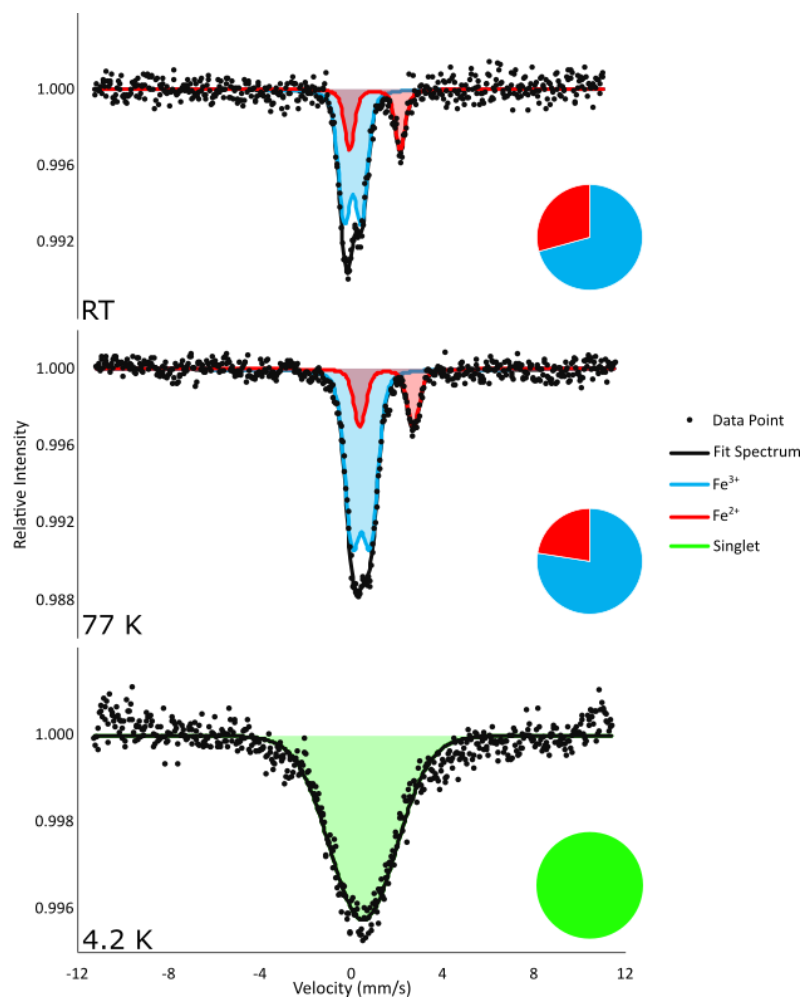


Figure 5.15 - Temperature dependent Mössbauer spectra of MN148 S005 01 with pie charts showing percentage of minerals identified

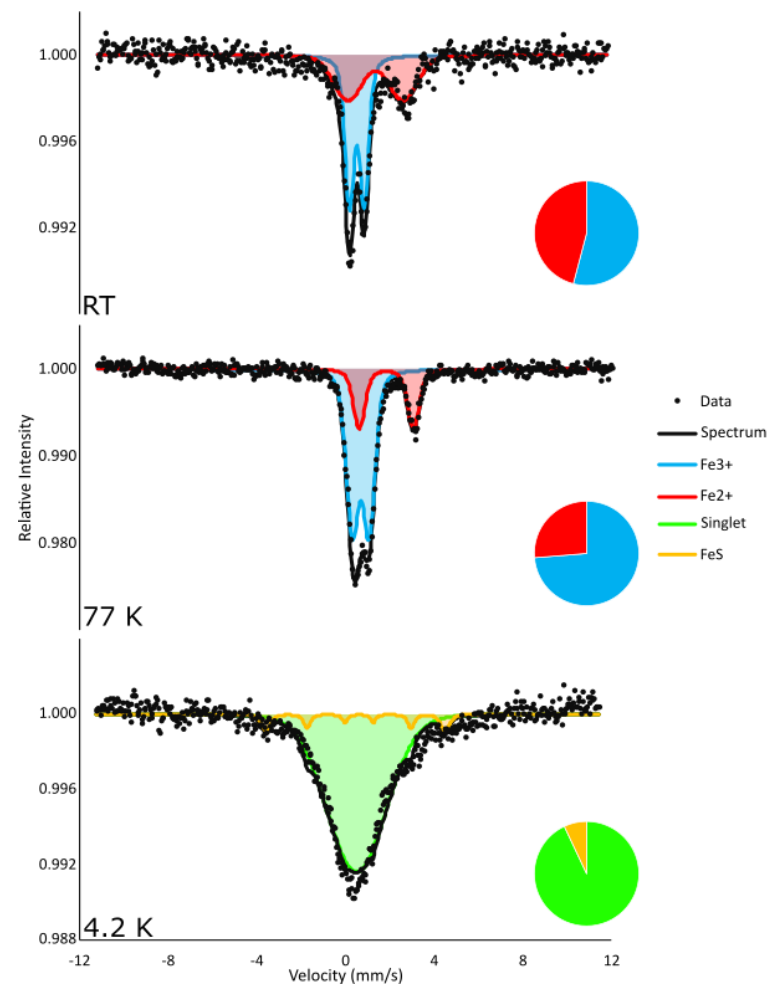


Figure 5.16 - Temperature dependent Mössbauer spectra of MN148 S005 29 with pie charts showing percentage of minerals identified

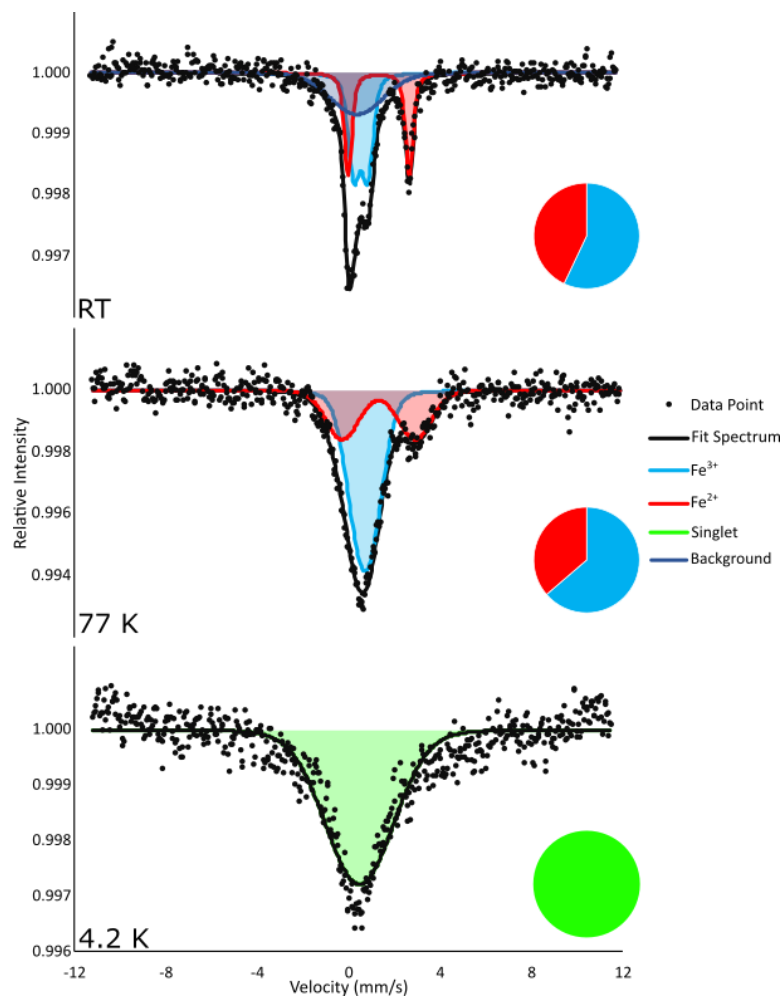


Figure 5.18 - Temperature dependent Mössbauer spectra of MN148 S006 01 with pie charts showing percentage of minerals identified

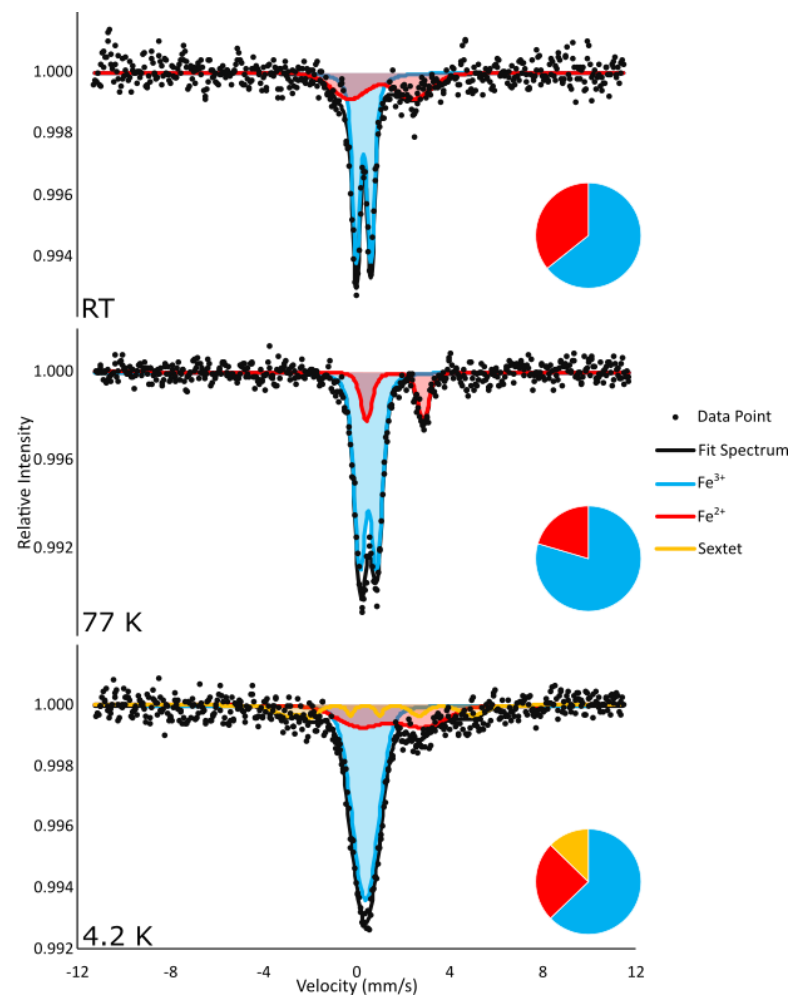


Figure 5.17- Temperature dependent Mössbauer spectra of MN148 S006 30 with pie charts showing percentage of minerals identified

Table 5.10 - Mössbauer spectra parameters of MN148 S004 01

Mineral Phase	δ (mm/s)	ΔE_Q or ε (mm/s)	$B_{hf}(T)$	Γ (mm/s or T)	Peak Area (%)	Temperature
Fe3+	0.34	0.62	-	0.43	76.1	RT
Fe2+	1.13	2.61	-	0.31	23.9	
Fe3+	0.36	0.76	-	0.94	50.0	77 K
Fe2+	0.96	2.40	-	1.93	50.0	
Singlet	0.53	0.09	-	3.57	100.0	4.2 K

Table 5.11 - Mössbauer spectra parameters of MN148 S004 33

Mineral Phase	δ (mm/s)	ΔE_Q or ε (mm/s)	$B_{hf}(T)$	Γ (mm/s or T)	Peak Area (%)	Temperature
Fe3+	0.33	0.60	-	0.34	74.4	RT
Fe2+	1.11	2.67	-	0.35	25.6	
Fe3+	0.49	0.75	-	0.81	67.5	77 K
Fe2+	1.1	3.13	-	1.17	32.5	
Singlet	0.44	0.00	-	2.28	92.1	4.2 K
Sextet	0.29	-0.21	25.0	0.90	7.9	

Table 5.12 - Mössbauer spectra parameters of MN148 S005 01

Mineral Phase	δ (mm/s)	ΔE_Q or ε (mm/s)	$B_{hf}(T)$	Γ (mm/s or T)	Peak Area (%)	Temperature
Fe3+	0.35	0.61	-	0.48	70.7	RT
Fe2+	1.11	2.54	-	0.37	29.3	
Fe3+	0.38	0.79	-	0.56	77.5	77 K
Fe2+	1.48	2.33	-	0.43	22.5	
Singlet	0.53	0.03	-	2.84	100.0	4.2 K

Table 5.13 - Mössbauer spectra parameters of MN148 S005 29

Mineral Phase	δ (mm/s)	ΔE_Q or ε (mm/s)	$B_{hf}(T)$	Γ (mm/s or T)	Peak Area (%)	Temperature
Fe3+	0.31	0.65	-	0.28	54.1	RT
Fe2+	1.13	2.46	-	1.18	45.9	
Fe3+	0.37	0.74	-	0.44	73.7	77 K
Fe2+	1.50	2.39	-	0.41	26.3	
Singlet	0.49	0.00	-	2.58	93.0	4.2 K
Sextet	0.52	-0.08	25.1	1.00	7.0	

Table 5.14 - Mössbauer spectra parameters of MN148 S006 01

Mineral Phase	δ (mm/s)	ΔE_Q or ε (mm/s)	$B_{hf}(T)$	Γ (mm/s or T)	Peak Area (%)	Temperature
Fe3+	0.37	0.60	-	0.38	38.5	RT
Fe2+	1.14	2.64	-	0.21	29.0	
Background	0.20	0.13	-	2.91	32.5	
Fe3+	0.47	0.66	-	1.00	63.7	77 K
Fe2+	1.06	3.12	-	1.31	36.3	
Singlet	0.46	0.02	-	2.89	100.0	4.2 K

Table 5.15 - Mössbauer spectra parameters of MN148 S006 30

Mineral Phase	δ (mm/s)	ΔE_Q or ε (mm/s)	$B_{hf}(T)$	Γ (mm/s or T)	Peak Area (%)	Temperature
Fe3+	0.30	0.63	-	0.20	64.3	RT
Fe2+	1.06	2.70	-	1.44	35.7	
Fe3+	0.37	0.72	-	0.39	79.6	77 K
Fe2+	1.5	2.41	-	0.37	20.4	
Fe3+	0.37	0.48	-	0.85	62.8	4.2 K
Fe2+	1.51	2.69	-	1.94	24.5	
Sextet	0.66	0.3	24.7	2.92	12.7	

MN148 S004 01, S005 01, S006 01

Samples S004 01, S005 01, and S006 01 were collected from clay at the top of collected cores from the Black Sea (Table 5.2). Room temperature Mössbauer spectroscopy revealed Fe^{2+} and Fe^{3+} doublets (Figure 5.13; Figure 5.15; Figure 5.18; Table 5.10; Table 5.12; Table 5.14). The Fe^{3+} doublet has similar parameters as pyrite, illite (Yoshida and Langouche, 2013) or the Fe_3D_3 doublet identified on Mars by the Opportunity rover (Morris et al., 2006a), classified in Chapter 3 as npOx. At 77 K there is no change in observed subspectra except for an increase in the isomer shift δ , (Yoshida and Langouche, 2013) and a change in area percentage of the doublets. The area percentage change is seen with an increased in Fe^{2+} to be equal to the amount of Fe^{3+} . The observed doublets at room temperature and 77 K are likely illite. At 4.2 K, a singlet dominates the spectrum. The singlet has a similar isomer shift to the iron sulfide mineral, however the large line width (Table 5.10; Table 5.12; Table 5.14) and lack of appearance at higher temperature spectra makes this an unlikely iron mineral in the mineralogy. The wide singlet at 4.2 K is more likely due to clay minerals beginning to undergo magnetic ordering but not completely, causing overlapping of various peaks that appear as one singlet.

MN148 S004 33, S005 29

Samples S004 33 and S005 29 were collected from clay at the base of collected cores from the Black Sea (Table 5.2). Room temperature and 77 K Mössbauer measurements are similar to those seen in the top of the core samples described above, however at 4.2 K, a sextet appears. The wide singlet at 4.2 K is more likely due to clay minerals beginning to undergo magnetic ordering but not completely, causing overlapping of various peaks that appear as one singlet. The sextet observed has small hyperfine fields ranging from 25.0–25.1 T (Table 5.11; Table 5.13), which are within the range of the iron sulfide mineral pyrrhotite (Yoshida and Langouche, 2013). As the sextet does not appear at room temperature, it could be assumed to be a poorly crystalline iron sulfide phase. The wide singlet that dominates the 4.2 K spectra makes full identification of the sextet difficult.

MN148 S006 30

Sample S006 30 was collected from the clay at the base of the S006 core from the Black Sea (Table 5.2). Room temperature and 77 K Mössbauer measurements are similar to those seen in the top of the core samples described above (Figure 5.17; Table 5.15). Unlike the other Black Sea samples, a singlet does not dominate the 4.2 K spectrum of S006 30 (Figure 5.17). Both doublets remain at 4.2 K, suggesting a more crystalline or homogeneous mineralogy within the

sample. The sextet that appears at 4.2 K is within the parameters for the iron sulfide mineral pyrrhotite (Yoshida and Langouche, 2013), but it is difficult to definitively confirm this due to the high signal-to-noise ratio of the spectrum.

Whitby (UK)

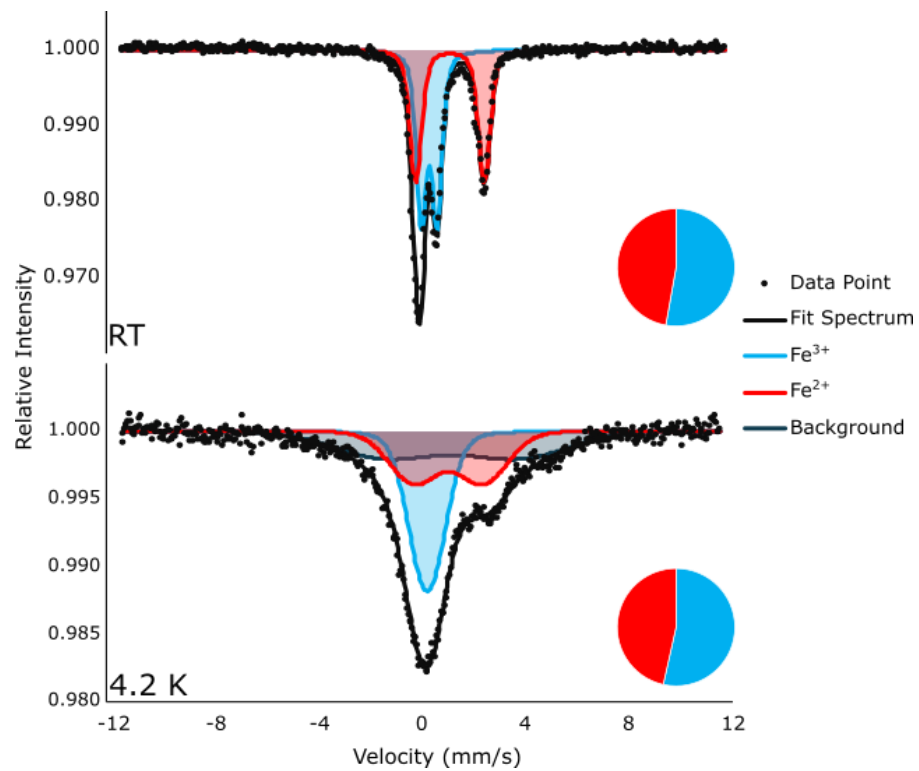


Figure 5.20 - Temperature dependent Mössbauer spectra of AlSh1 with pie charts showing percentage of minerals identified

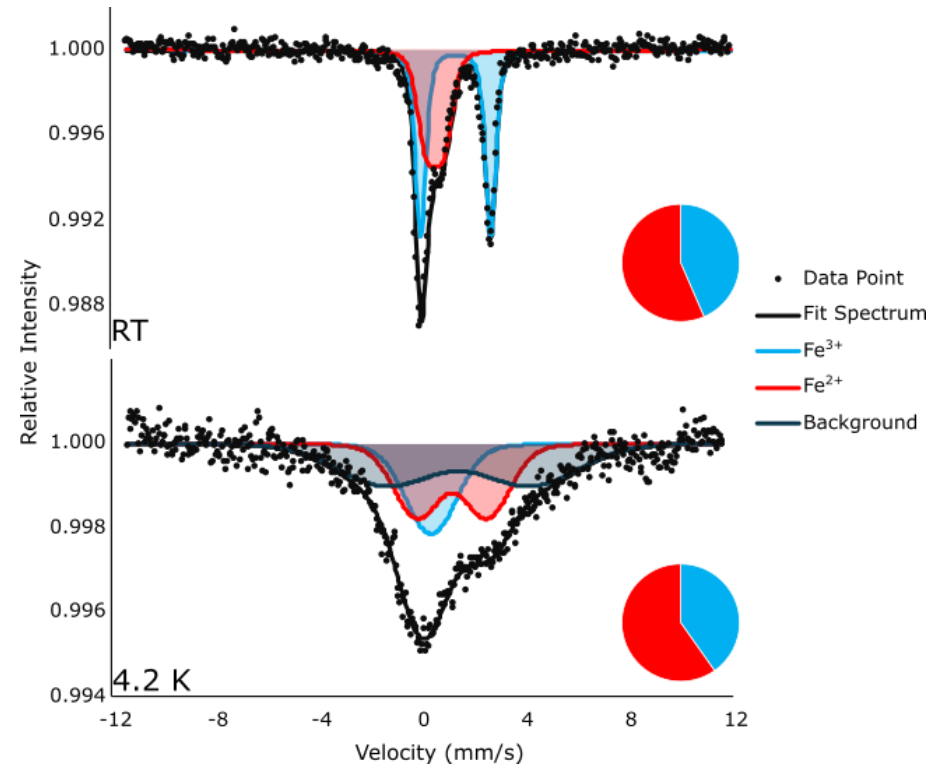


Figure 5.19 - Temperature dependent Mössbauer spectra of AlSh2 with pie charts showing percentage of minerals identified

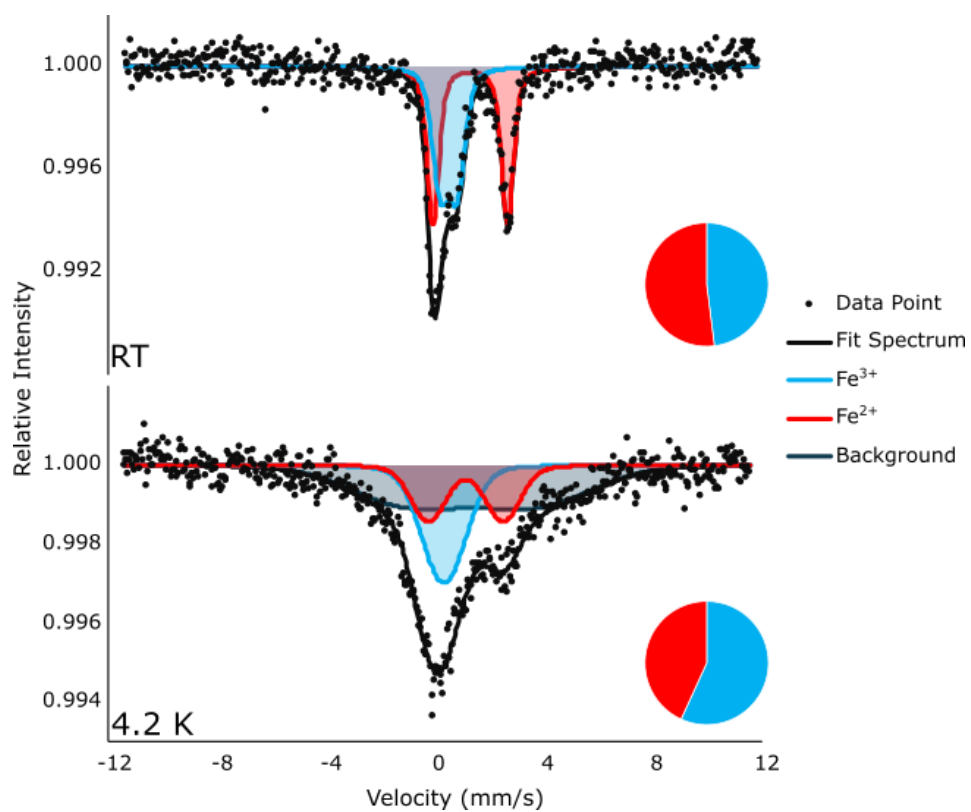


Figure 5.21 - Temperature dependent Mössbauer spectra of AlSh3 with pie charts showing percentage of minerals identified

Table 5.16 - Mössbauer spectra parameters of the Alum Shale mudstone samples

Sample	Phase	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	Peak Area (%)	Temperature
AlSh1	Fe3+	0.31	0.60	0.28	52.8	RT
	Fe2+	1.11	2.61	0.35	47.2	
	Fe3+	0.31	0.60	1.06	35.9	4.2 K
	Fe2+	1.11	2.61	1.76	31.2	
	Background	1.24	5.01	5.01	32.9	
AlSh2	Fe3+	0.34	0.65	0.58	43.5	RT
	Fe2+	1.13	2.66	0.29	56.5	
	Fe3+	0.34	0.65	1.69	23.9	4.2 K
	Fe2+	1.13	2.66	1.65	35.5	
	Background	1.36	5.50	3.55	40.6	
AlSh3	Fe3+	0.35	0.61	0.43	48.0	RT
	Fe2+	1.14	2.71	0.27	52.0	
	Fe3+	0.35	0.61	1.32	29.2	4.2 K
	Fe2+	1.14	2.71	1.13	22.2	
	Background	1.36	4.61	4.04	48.6	

AlSh1, AlSh2, AlSh3

Samples AlSh1, AlSh2, and AlSh3 were collected from various points along the coastline at Whitby, UK (Figure 5.4). Room temperature Mössbauer spectroscopy observed two doublets in all three samples identified as Fe^{3+} and Fe^{2+} , all with similar parameters (Table 5.16). As the temperature is decreased to 4.2 K, little change is observed with the Mössbauer parameters of each sample except for the appearance of a background phase. The Fe^{3+} doublet has parameters within the range for the Fe3D3 doublet identified on Mars by the Opportunity rover (Morris et al., 2006a), classified in Chapter 3 as npOx. However, the doublet is more likely to belong to a clay mineral, not npOx due to the lack of iron oxides in the 4.2 K spectra (Figure 5.20; Figure 5.19; Figure 5.21). Both the doublets in the room temperature spectra of all the samples are likely to be due to illite and pyrite (Yoshida and Langouche, 2013). The presence of illite is also confirmed by the presence of the wide background doublet at 4.2 K in all the samples, where clay minerals begin to undergo magnetic alignment but not fully (Murad, 1998), causing overlapping of various peaks and results in the appearance of the background doublet. The lack

of superparamagnetism in any of the Fe^{3+} doublets suggest an absence of reactive iron in the form of npOx.

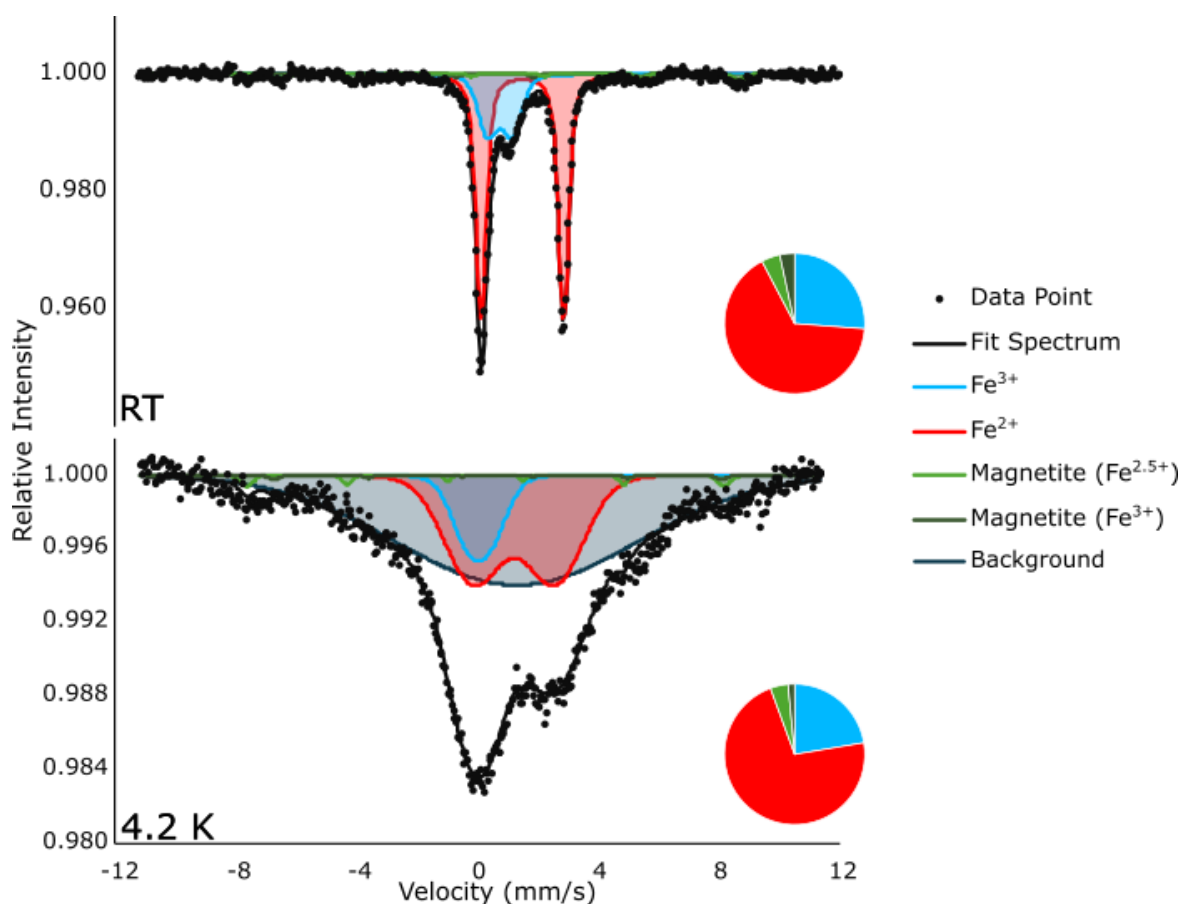


Figure 5.22 - Temperature dependent Mössbauer spectra of the Haggis Rock with pie charts showing percentage of minerals identified

Table 5.17 - Mössbauer spectra parameters of the Haggis Rock

Mineral Phase	δ (mm/s)	ΔE_Q or ϵ (mm/s)	B_{hf} (T)	Γ (mm/s or T)	Peak Area (%)	Temperature
Fe3+	0.41	0.79	-	0.52	26.2	RT
Fe2+	1.13	2.66	-	0.22	66.1	
Magnetite (Fe ³⁺)	0.26	0.00	49.0	1.00	4.3	
Magnetite (Fe ^{2.5+})	0.67	0.00	46.0	1.00	3.4	
Fe3+	0.04	0.81	-	0.99	9.0	4.2 K
Fe2+	1.21	2.69	-	1.85	29.0	
Magnetite (Fe ³⁺)	0.26	0.00	49.0	1.00	1.7	
Magnetite (Fe ^{2.5+})	0.67	0.00	46.0	1.00	0.6	
Background	1.30	0.01	-	7.95	59.7	

Room temperature Mössbauer spectroscopy of the Coulter Quarry sample revealed the presence of two doublets and two sextets which are identified as magnetite (Figure 5.22). As the temperature is decreased to 4.2 K, a background feature appears, whilst the other peaks remain at similar percentages relative to each other (Table 5.17), suggesting the background doublet to be just background noise. Proper identification of the doublets is difficult without analysis with other instruments. The lack of superparamagnetism of either of the Fe^{3+} doublet suggests an absence of npOx.

5.4.2. X-Ray Diffraction (XRD)

X-Ray diffraction (XRD) identifies mineral structures within a sample. See Chapter 2 for analysis method.

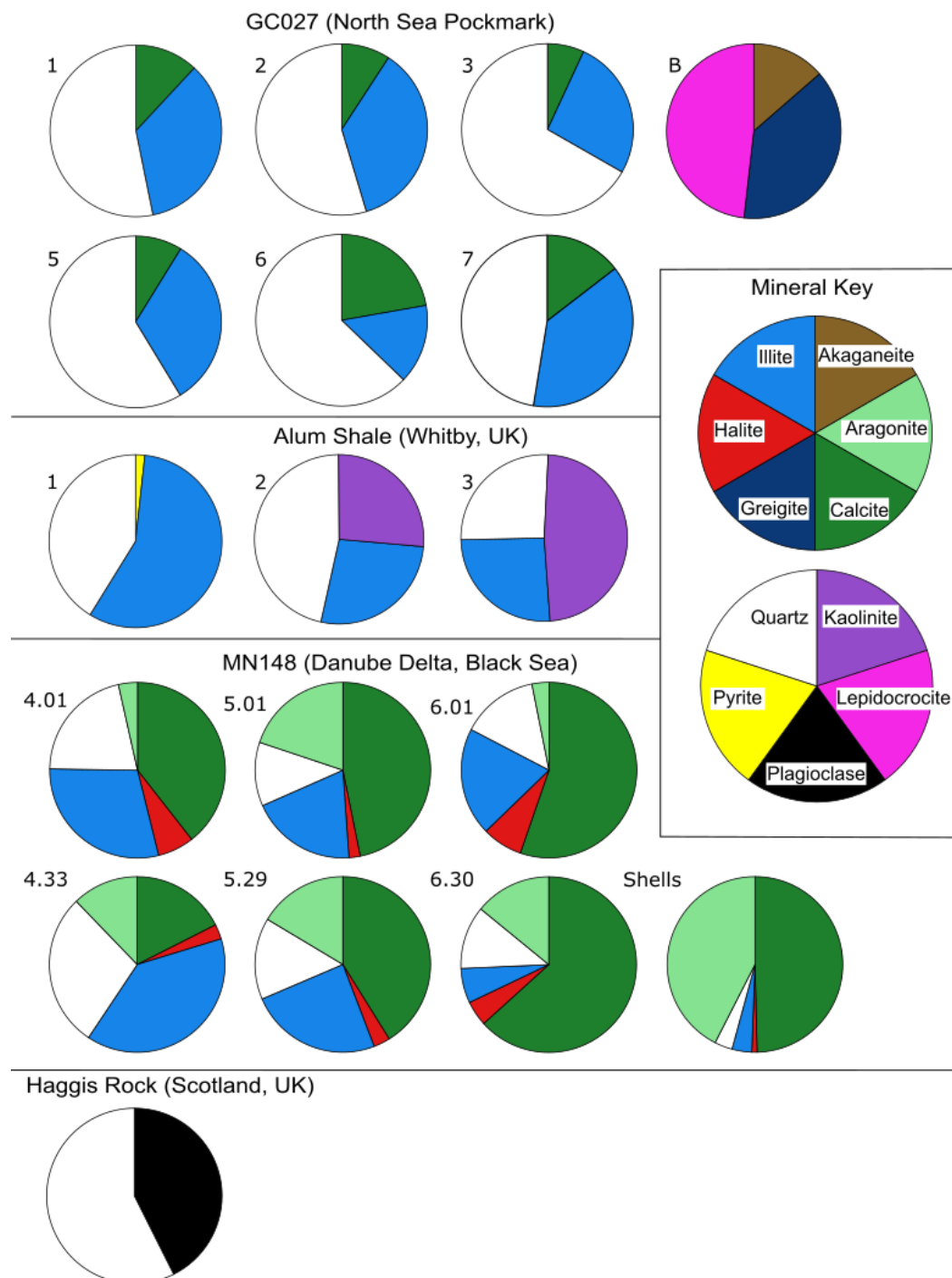


Figure 5.23 - Pie charts showing mineralogy percentages of samples analysed with XRD

North Sea Pockmark (UK)

XRD measurements of samples GC027 01, 02, 03, 05, 06 and 07 showed the presence of quartz, calcite and illite in varying percentages (Figure 5.23). Quartz is the dominate phase, followed by illite then calcite in all samples except GC027 06 which has greater amounts of calcite than illite. XRD measurements of sample GC027 B showed the presence of lepidocrocite, greigite and akaganeite (Figure 5.23).

Danube Delta/Black Sea (Romania)

XRD measurements of samples from the Danube Delta showed the presence of calcite, illite, quartz, aragonite and halite in varying percentages (Figure 5.23). The shells within the samples are composed of calcite and aragonite and are the likely source of mineral peaks identified within the other samples.

Whitby (UK)

XRD measurements of sample AlSh1 show the presence of illite, quartz and pyrite (Figure 5.23). Samples AlSh2 and AlSh3 do not contain pyrite, but are composed of quartz, illite and kaolinite.

Coulter Quarry (UK)

XRD measurements of the Haggis Rock shows the presence of only quartz and plagioclase (Figure 5.23).

5.4.3. Raman Spectroscopy

Raman spectroscopy is able to identify both mineralogy and organic molecules. Only select GC027 samples and AlSh2 were able to be analysed with Raman spectroscopy due to the characteristics of the other samples causing difficulties, such as the darkness of the sample or fluorescence due to the presence of iron oxides (Hanesch, 2009). The method is described in Chapter 2 and difficulties previously discussed and analysed in Chapter 4.

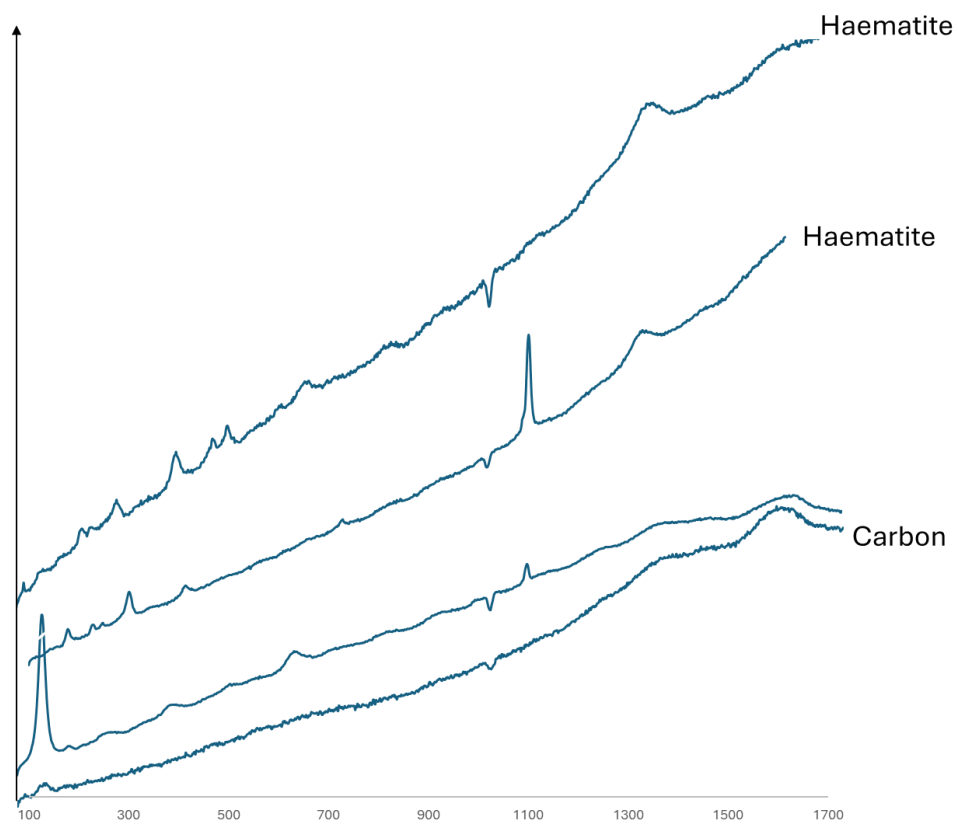


Figure 5.24 - Raman spectra of samples GC027 01 and 02

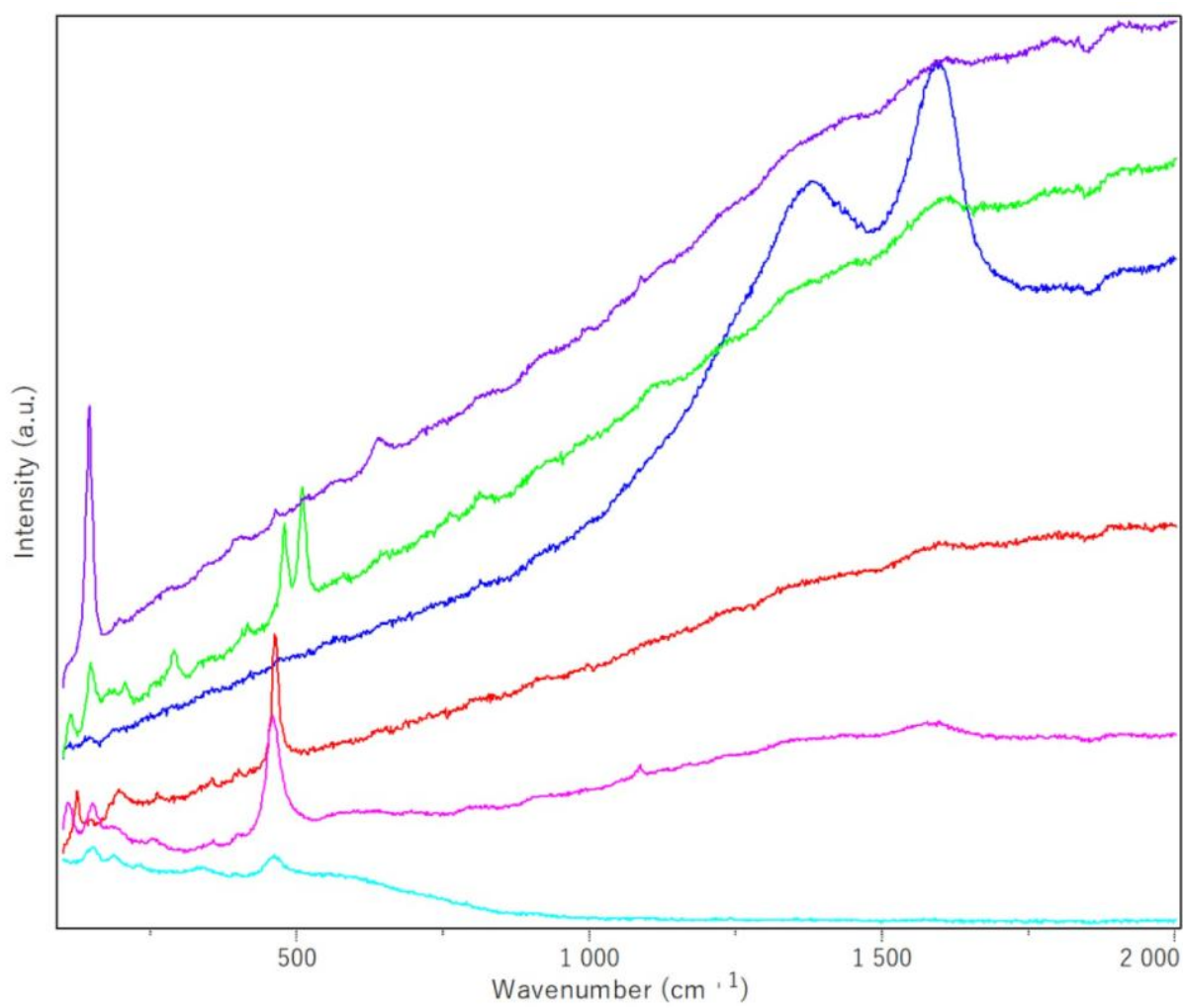


Figure 5.25 - Raman spectra of sample GC027 05

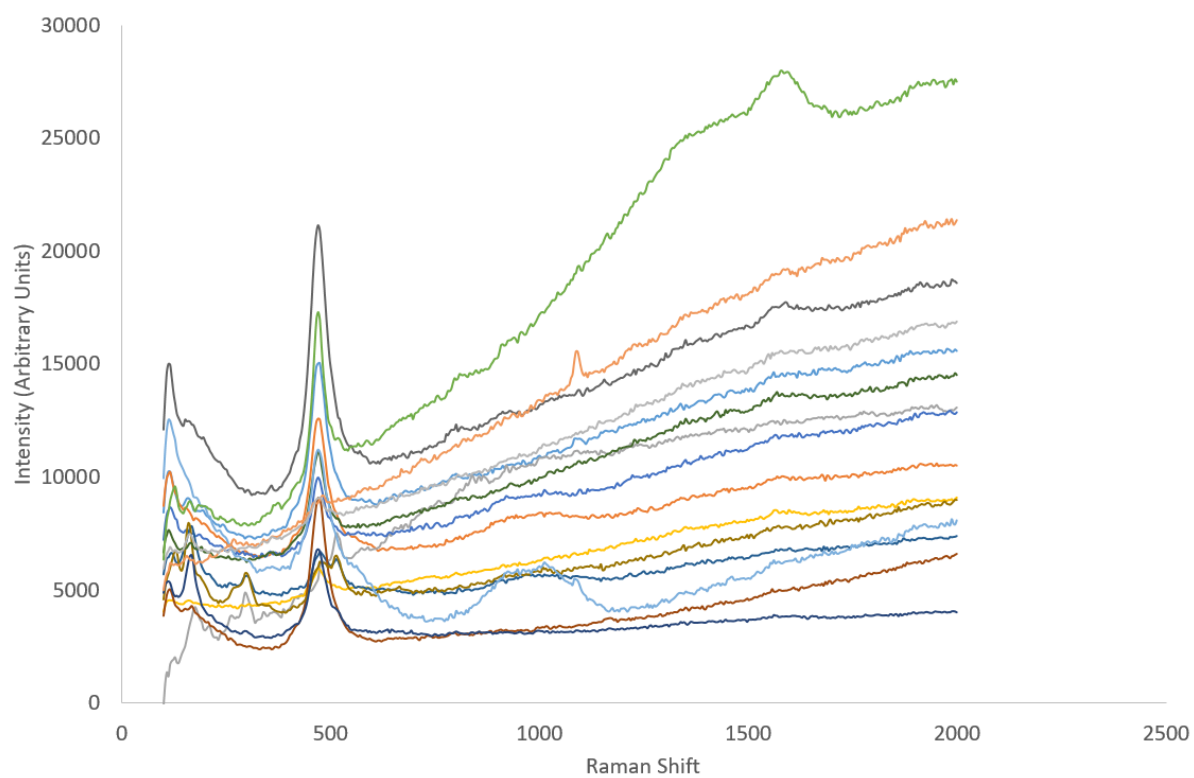


Figure 5.26 - Raman spectra of sample GC027 06

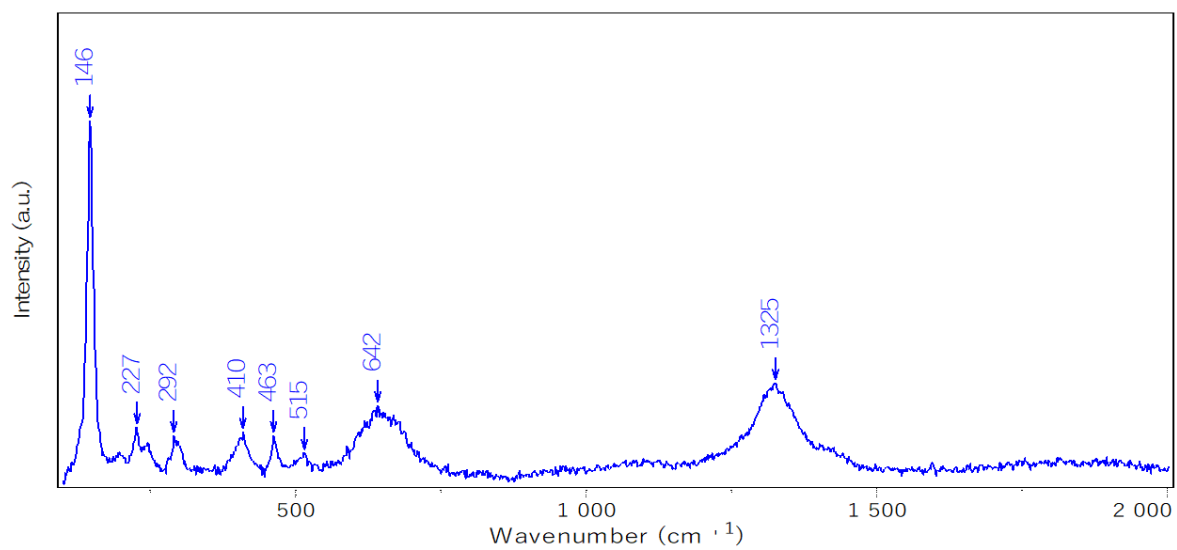


Figure 5.27 - Raman spectrum of sample GC027 07

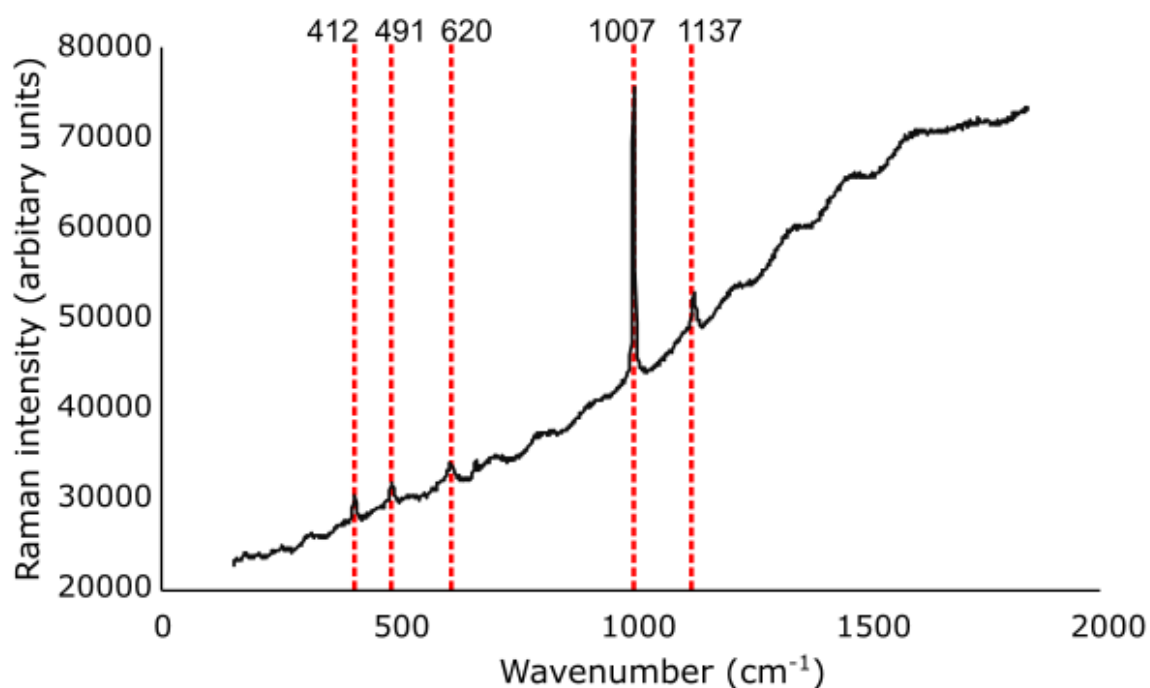


Figure 5.28 - Raman Spectrum of sample AlSh2. Peaks are highlighted with red dashed lines.

Table 5.18 – Minerals and organics detected by Raman spectroscopy of some North Sea Pockmark samples and an Alum Shale mudstone sample.

Sample	Mineralogy
GC027_01	Molecular carbon
GC027_02	Haematite, molecular carbon
GC027_05	Molecular carbon, feldspar, quartz
GC027_06	Carbonate, quartz, phosphate, feldspar, molecular carbon
GC027_07	Carbonate, quartz, phosphate, feldspar, anatase and haematite
AlSh2	Pyroxene

Raman spectroscopy was capable of detecting molecular carbon within several of the North Sea Pockmark samples (Table 5.18). The common rock forming minerals such as quartz and feldspar were detected along with haematite, carbonate, phosphate and anatase (Figure 5.24; Figure 5.25; Figure 5.26; Figure 5.27)

In the Alum Shale mudstone 2 sample, only pyroxene was detected (Figure 5.28).

5.4.4. Inductively coupled plasma optical emission spectroscopy (ICP-OES)

Inductively coupled plasma optical emission spectroscopy was used to gain elemental information of the samples post extraction and microwave digestion following the protocol described in Chapter 2. Na, K, Ca, Mg, Fe, Mn, Co, Ni, Al, P, and Si were all measured during this process. Measurements were normalised to each other to give percentages, with Fe, Al, and Si focused on within this chapter, with results below plotted using the ggtern package in R (Hamilton and Ferry, 2018).

North Sea Pockmark (UK)

ICP-OES analysis of the North Sea Pockmark samples shows varied chemistry throughout the core (Figure 5.29). Only sample GC027 1 shows a loss of Fe in both extracted samples compared to the control sample, whilst the other samples generally show no trend except for the control samples containing more Si.

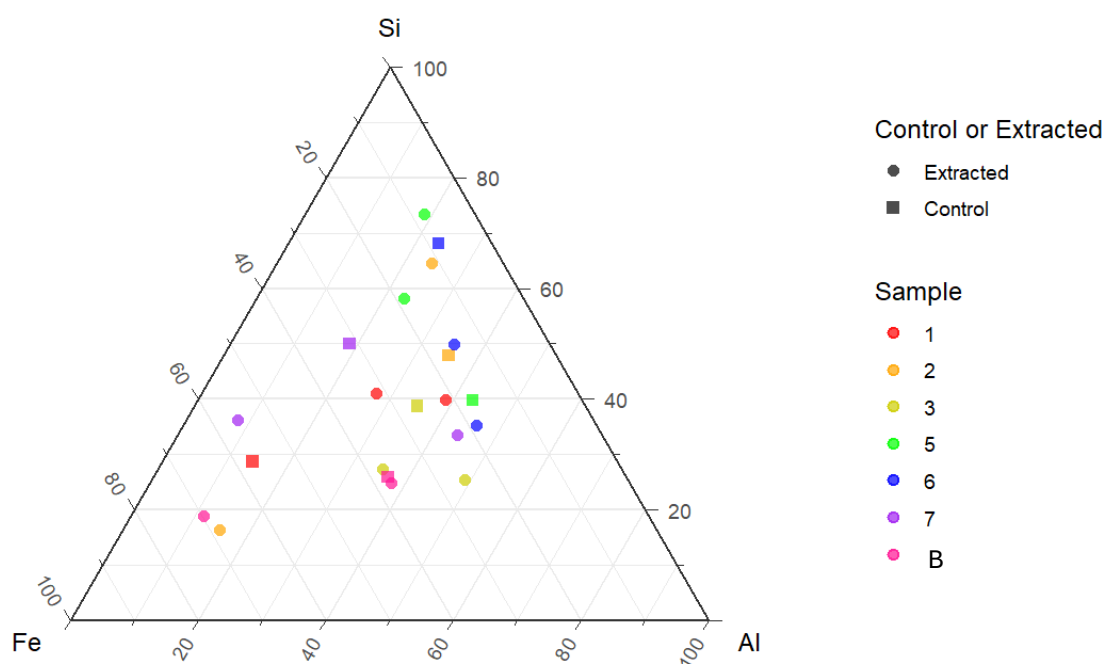


Figure 5.29 - Si-Fe-Al ternary diagram showing ICP-OES measurements from the North Sea Pockmark samples.

Danube Delta/Black Sea (Romania)

ICP-OES analysis of the Danube Delta/Black Sea samples shows that the samples are always >30% Fe (Figure 5.30). Sample S005 01 and S006 30 show a loss of Fe in the extracted samples

when compared to the control samples, whilst the other samples generally show no trend except for the control samples containing more Si.

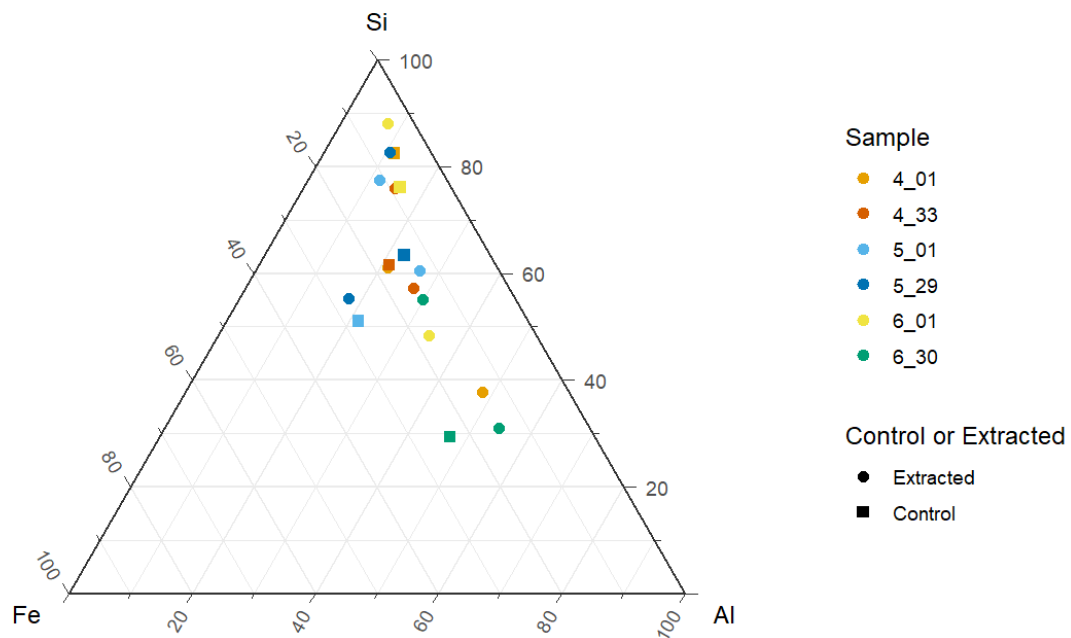


Figure 5.30 - Si-Fe-Al ternary diagram showing ICP-OES measurements from the Danube Delta/Black Sea samples.

Whitby (UK)

ICP-OES analysis of the Alum Shale mudstone samples shows that the samples are always >30% Fe (Figure 5.31). Sample 2 shows no trend when comparing the control and extracted

samples. Samples 1 and 3 control samples contain more Al than their extracted counterparts.

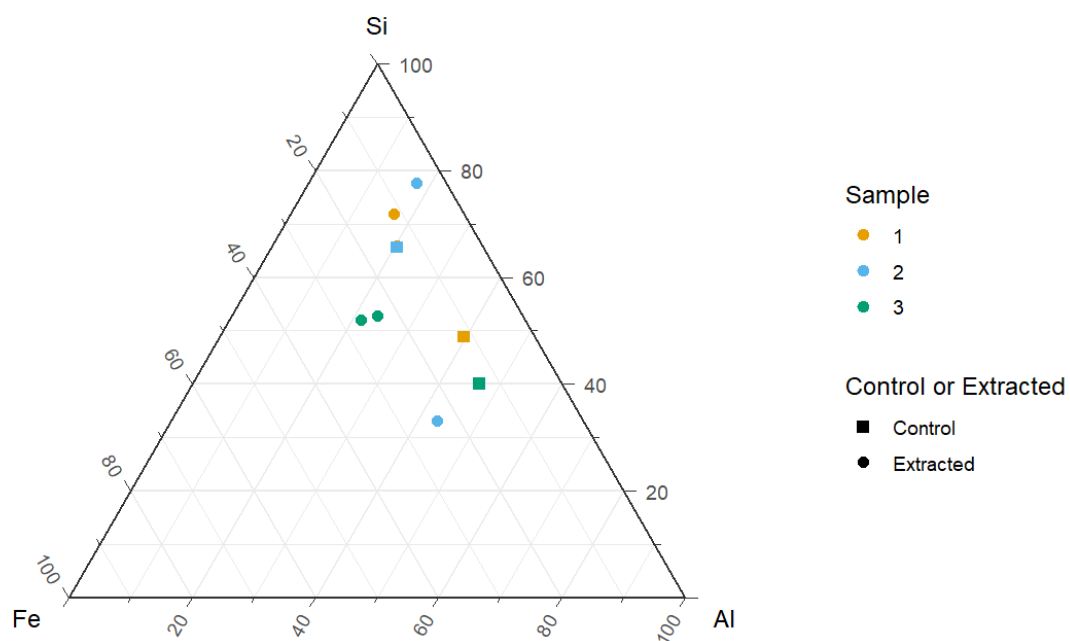


Figure 5.31 - Si-Fe-Al ternary diagram showing ICP-OES measurements from the Alum Shale mudstone samples.

Coulter Quarry (UK)

ICP-OES analysis of the Haggis Rock shows the control sample contains more Al than the extracted samples (Figure 5.32).

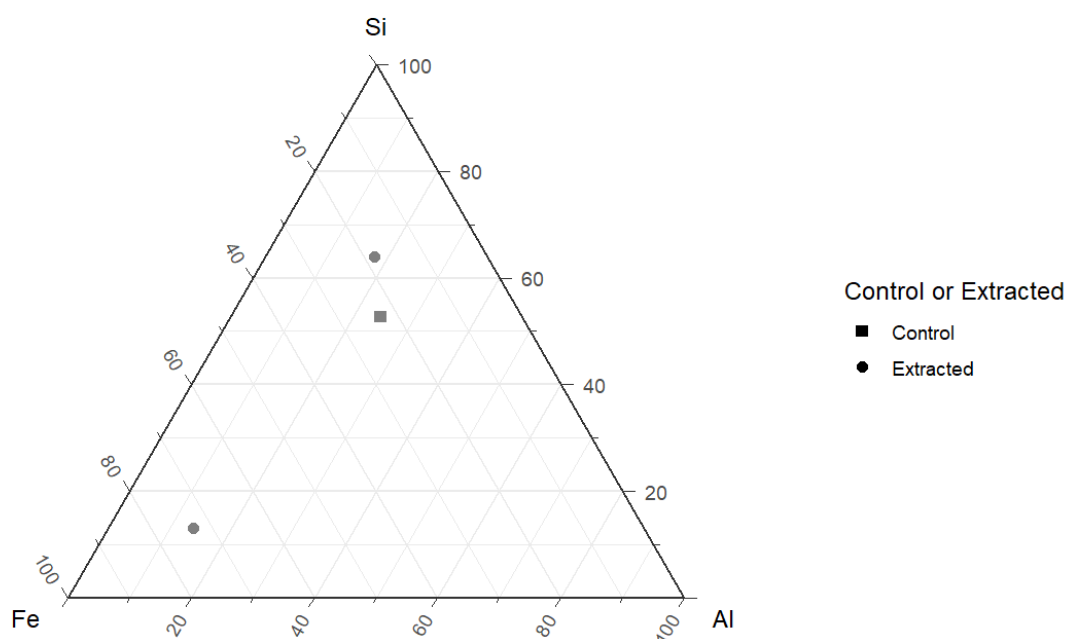


Figure 5.32 - Si-Fe-Al ternary diagram showing ICP-OES measurements from the Haggis Rock samples.

5.4.5. Total Carbon/Total Nitrogen

Total Carbon/Total Nitrogen (C/N) analysis was carried out on the both the extracted and control samples described above. This was done to understand the amount of carbon bound to reactive iron species.

North Sea Pockmark (UK)

GC027 7 control sample was not analysed due to a lack of sample. C/N analysis of the North Sea Pockmark samples shows a positive correlation between the two elements. Sample GC027 1 control has more carbon than the extracted samples. None of the other analysed samples shows this relationship, with samples GC027 3, 5 and B controls containing less carbon than their extracted counterparts (Figure 5.33).

Danube Delta/Black Sea (Romania)

C/N analysis of the Danube Delta/Black Sea samples shows a positive correlation between the two elements. All samples show greater amounts of carbon in the control samples than the residue left from extracted samples, however sample S004 01 also shows a decrease of nitrogen in the control sample (Figure 5.33).

C/N analysis of the Alum Shale mudstone shows a positive relationship between the 2 elements. All the control samples contain more carbon than the extracted samples (Figure 5.33).

Haggis Rock (UK)

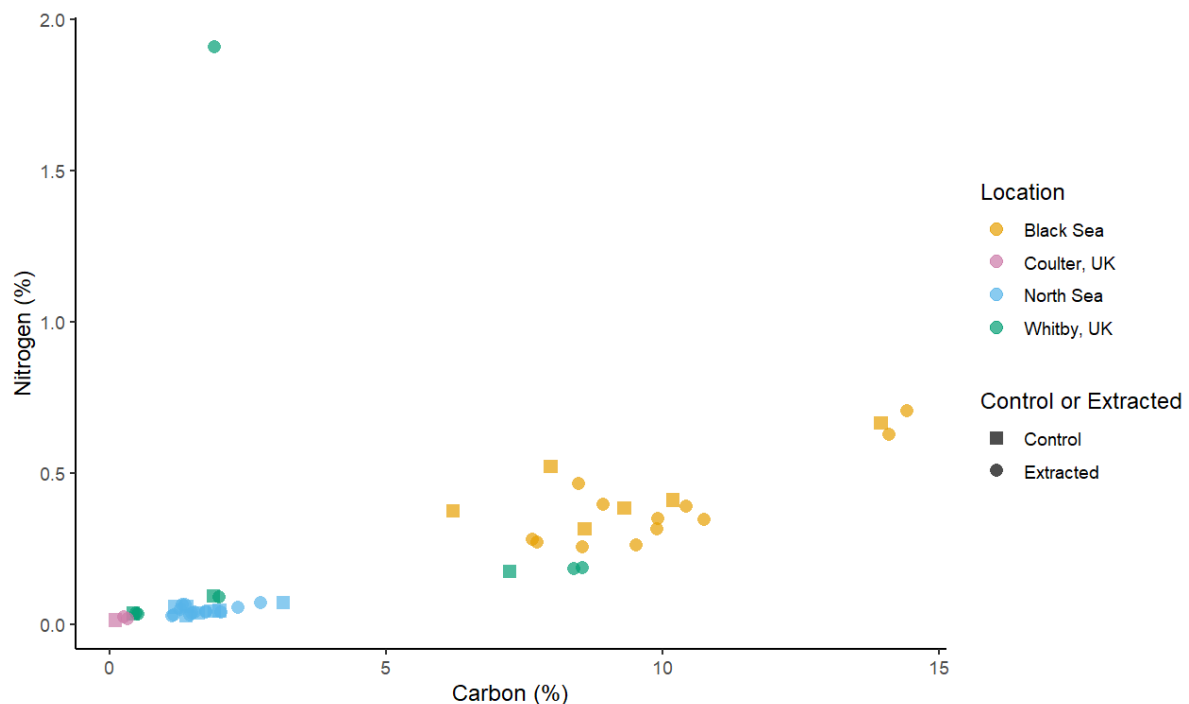


Figure 5.33 - Graph showing carbon to nitrogen values for samples from the North Sea, Black Sea, Whitby (UK) and Coulter Quarry (UK)

5.5. Discussion

Analogue sites were selected predominantly by ease of access, with both the North and Black Sea samples belonging to past PhD students within the University of Stirling, used with permission. The Whitby samples were collected during a family holiday and the Coulter Quarry sample during a fieldtrip. Whilst none of the sites were primarily selected for how similar they are to Mars; it should be noted that fieldwork was heavily restricted due to the COVID-19 pandemic resulting in a limitation in sample selection. However, characteristics of the sites reflect features observed on Mars and inferred chemical environments, categorising them as

first and second order analogues. The main aim of analysing the selected samples was not how good analogues they are, but for them to be analysed by different techniques onboard the Mars rovers; identifying how reactive iron species might be observed by these techniques.

5.5.2. Mineralogical Instruments

North Sea Pockmark (UK)

Mössbauer spectroscopy of samples from the Scanner Pockmark show a wealth of different iron minerals including: greigite, lepidocrocite, goethite and akaganeite. XRD was only able to detect some of these iron minerals in sample GC027 B whilst in all the other only quartz, calcite and illite were detected. This is likely due to the iron minerals being so fine grained in most of the samples, making them X-ray amorphous and thus undetectable by XRD. The North Sea Pockmark samples are some of the only samples able to be analysed by Raman spectroscopy within this study. In most samples, carbon was detected. Samples GC027 05-07 all had quartz detected by both XRD and Raman spectroscopy. Raman spectroscopy also detected other mineralogy such as carbonate, phosphate, feldspar and anatase in samples GC027 05-07 which were not seen by the other techniques. In samples GC027 02 and 07, Raman spectroscopy detected haematite which is not seen by Mössbauer spectroscopy. As Mössbauer spectroscopy did not detect haematite in these samples, it can be assumed laser damaged occurred during Raman analysis resulting in the transformation of iron minerals within the samples. This damage is previously discussed in Chapter 4. Reactive iron species (npOx) are only observed in samples GC027 01 and 07.

Analysis of samples GC027 07 and B shows differences between the nodules within the core. Mössbauer spectroscopy showed GC027 07, and B are both composed of greigite and lepidocrocite, whilst only B contains akaganeite. However, XRD did not detect any iron minerals in GC027 07, suggesting that the iron minerals were too fine grained and thus amorphous to be detected. As GC027 07 was brown in colour, whilst B was black in colour, it can be assumed that 07 was exposed to the air causing the iron to oxidise and rust, whereas B remained reduced. This suggests that exposure to air caused a loss of magnetism and the breakdown of crystals to become fine grained.

Danube Delta/Black Sea (Romania)

Raman spectroscopy was incapable of detecting mineralogy without visible burning (smoke) of the sample occurring. Mössbauer spectroscopy detected Fe^{3+} and Fe^{2+} doublets that aligned with illite parameters, which was also detected with XRD. XRD also detected quartz, halite, calcite and aragonite. Due to XRD analysis of just the shells from the cores, it can be assumed that the calcite and aragonite originate from the shell debris in the samples. XRD analysis did not identify the unknown mineral that caused the sextets in the 4.2 K Mössbauer measurements of sample S004 33, S005 29 and S006 30, suggesting that it is amorphous material that cannot be fully quantified.

Alum Shale Mudstone (UK)

Mössbauer spectroscopy detected Fe^{3+} and Fe^{2+} doublets within the Alum shale samples which are likely to be due to iron bearing clays. XRD was able to detect illite along with quartz in all samples and kaolinite within AlSh 2 and 3. Only AlSh 1 had pyrite detected by XRD, which is also be in the Mössbauer spectra. Raman spectroscopy of AlSh 2 was successful due to it being lighter in colour than the other 2 samples. Only pyroxene was detected with Raman spectroscopy which was not observed with the other samples.

Haggis Rock (UK)

Fe^{3+} , Fe^{2+} and magnetite were detected by Mössbauer spectroscopy, whilst XRD only detected quartz and plagioclase with Raman spectroscopy not able to gain any information on the sample.

What this means for Mars results

Different instruments detect different things, not only that some instruments struggle to detect minerals that others do.

Mössbauer spectroscopy is a powerful technique for analysing iron mineralogy, however it does have some drawbacks. The main factor being that it can only detect minerals that contain ^{57}Fe . Within this study, it is also seen that analysing samples containing iron-clays within their mineralogy causes wider peaks to appear within the Mössbauer spectra. This often occurs due to the clays being polymineralic, iron-poor and only a few iron-rich clays magnetically align above 4.2 K (Murad, 1998). The wide clay peaks obscure other iron minerals, making identification troublesome. To fully understand the whole mineralogy of a sample, other analytical techniques are needed to be used.

XRD can identify a wide range of minerals within a sample, however, is unable to detect X-ray amorphous material. X-ray amorphous material can be inferred with XRD, occurring as a wide peak within the XRD pattern. The chemical nature of the wide peak is difficult to identify without in-depth analysis that requires additional information from other instruments. Samples rich in iron oxides also pose an issue for XRD analysis with sample GC027 B needing a longer scan time to reduce noise and allow for mineral identification compared to the other samples. Iron minerals are generally not detected by XRD, for example the Haggis sample is known to contain magnetite from Mössbauer spectroscopy, but XRD only detected quartz and plagioclase. Raman spectroscopy is capable of analysing both mineralogy and organic material but is seen here to struggle with iron oxide identification, often causing dehydration into haematite which could lead to the destruction of any organic carbon bound to the reactive iron species. This problem needs to be addressed for ESA's ExoMars Rover, *Rosalind Franklin*, as the Raman Laser Spectrometer (RLS) is used on the sample before being deposited into the Mars Organic Molecule Analyser (MOMA). Identification of organic molecules with the MOMA instrument is further complicated by the obtained data needs to be combined with RLS data for accurate identification (Goesmann et al., 2017). Iron oxides within the sample can both destroy bound organic matter and to overwhelm the Raman spectrum with fluorescence. This chain of events could erase any evidence of life that the ExoMars rover might analyse. Preserving any organic carbon is paramount in the effort to determine whether there was ever life on Mars.

Mineralogical instruments sent to the Martian surface onboard the MER, MSL and Mars 2020 rovers include Mössbauer spectroscopy, XRD and Raman spectroscopy. Each technique has drawbacks which is seen when using them to analyse the Martian analogues here. Due to payload limits on future rovers, it is not feasible to have a selection of different mineralogical instruments onboard. Difficulty in analysis of a sample with only one mineralogical instrument highlights the importance of sample return, allowing for full understanding of extraterrestrial geological processes.

5.5.3. Extractions

ICP-OES analysis shows varied elemental chemistry between each sample suite. Extracted samples that contain less Fe than their control counterparts are of importance here as that shows a loss of iron during the extraction process. Samples GC027 1, S005 01 and S006 30 are the only samples to exhibit a loss of Fe during the extractions. All 3 of these samples also showed a loss of carbon post-extraction suggesting the presence of reactive iron bound to

carbon only in those samples. Meaning the npOx detected in sample GC027 7 was not bound to carbon. the Danube Delta/Black Sea samples did not have npOx detected by any mineralogical tool but did have iron and carbon extracted in some samples. The lack of npOx detection with Mössbauer spectroscopy is likely due to the wide low temperature features obscuring evidence of npOx or the extraction targeted another iron phase during removal.

The Haggis Rock control sample contain very low amounts of carbon, potentially suggesting some contamination during extraction resulting in the extracted samples containing more, albeit very low, amounts of carbon. Overall, it is difficult to detect npOx in these selected samples and even harder to find evidence that their helping preserve organic matter.

5.6. Conclusions

This study demonstrates that terrestrial analogue investigations provide essential context for interpreting mineralogical and geochemical data acquired by Mars rovers. The comparative analysis of Mössbauer spectroscopy, XRD, Raman spectroscopy, and sequential extraction techniques shows that each method has unique strengths and limitations, and that integration of multiple approaches is vital for accurate mineral identification and assessment of organic preservation potential.

Mössbauer spectroscopy is highly adept at iron mineral identification, however problems may occur due to obstruction of peaks due to iron containing clays along with the limitation to only identifying minerals containing ^{57}Fe . XRD is good for overall mineral assemblage, however, is unable to see X-ray amorphous material which prevents confident identification of reactive iron species or other nanophase materials such as glass. It is also observed that samples high in iron oxides are difficult to analyse with XRD, with noisy patterns being produced unless longer acquisition times are used (as seen with sample GC027 B). Raman spectroscopy is capable of analysing both minerals and organic compounds but struggles if the sample is not ideal such as, light in colour or in a more crystalline phase (see Chapter XX). Iron oxides are not fully correctly identified with Raman spectroscopy or XRD within this chapter. Mars is known to be iron rich, highlighting current problems with results from the Martian surface.

Carrying out sequential extractions targeted on reactive iron bound to carbon is only successful in few samples, suggesting either the occurrence of reactive iron species does not always mean the preservation of organics or showcases flaws within sample site selection.

From a mission-planning perspective, the findings highlight the importance of recognising and mitigating instrument limitations before deploying them to Mars. For example, fluorescence

interference and laser-induced alteration in Raman spectroscopy could obscure biosignatures or alter mineralogical evidence, while the inability of XRD to directly detect amorphous phases risks underrepresenting key components of the Martian regolith. The interplay between reactive iron phases and organic matter preservation remains complex, with implications for biosignature detection strategies on Mars.

Future problems with ESA's ExoMars rover, *Rosalind Franklin*, RLS and MOMA instruments have been highlighted. Reactive iron species have the potential to both destroy bound organic matter and overwhelm the Raman spectrum with fluorescence. More work on this matter is needed to fully understand both the impacts this has for rover data from Mars and the preservation of carbon on Earth and Mars. A particular focus needs to be placed on identifying reactive iron species with different mineralogical techniques to prevent potential destruction of bound organic carbon.

Ultimately, understanding Mars' geological history and its potential to preserve evidence of past life will require a coordinated approach: targeted rover investigations, robust Earth-based analogue research, and, critically, the return of carefully selected Martian samples for comprehensive laboratory analysis. The work presented here represents one step towards that goal, underscoring that while analogue studies can never perfectly replicate Martian conditions, they remain one of our most powerful tools for preparing to interpret results from the Martian surface.

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6. Using Mössbauer Spectroscopy to understand iron mineralogy of carbonaceous meteorites.

6.1. Introduction

Before the Solar System formed as it is now, it was originally part of an interstellar cloud, formed of dust and gases (such as hydrogen). Gravitational instability (for example, shockwave from a supernova event) causes the collapse of the interstellar cloud, causing a hot dense core to form. The core has gravity, causing more gas and dust to collapse into the core. This collapse causes the core to get even hotter and denser which in turn means more dust and gas collapses into the core. This continues until the core is at a high enough temperature and density to begin nuclear fusion and become a star. It's estimated that ~99.9% of all the material in the region is drawn into the core for star formation, whilst the remaining ~0.1% forms what is known as a protoplanetary disk, which orbits the newly formed star. As the material cools, minerals start to form near the star whilst ice forms further away. Further cooling results in the coalescing of material which will eventually go on to form planets. Remaining material became asteroids. Asteroids preserve evidence of how the Solar System formed; with their mineralogy and spectral features being heavily studied. Pristine asteroid material has been retrieved by spacecraft and returned to Earth for study (Hayabusa 1, Hayabusa 2 and, Osiris-Rex), however this is an expensive process that can take several years. Another way to study the early Solar System is to look at meteorites. Meteorites are fragments of extraterrestrial bodies like asteroids, Mars or the Moon that have fallen to the Earth, allowing for the study of extraterrestrial materials without having to leave Earth. Meteorites have brought organics and water to Earth's surface that are thought to have helped to start life (Bischoff et al., 2021; Lipschutz and Schultz, 2014)

Meteorites are grouped according to their mineralogy. The carbonaceous chondrite (CC) group of meteorites are used in this study as they contain organic matter. Understanding the iron mineralogy of CC meteorites is important for a number of reasons:

1. Iron minerals can play an important role in the evolution of organic matter during alteration processes (Holm et al., 2015).

2. Some studies show evidence of the organic molecules being associated with iron oxide minerals in CC meteorites (Amri et al., 2005; Noun et al., 2019).
3. If meteorites are not collected immediately after their fall to Earth, terrestrial weathering processes alter mineralogy. Iron minerals are susceptible to weathering making them good indicators of the level of alteration the meteorite might have undergone on Earth's surface.

This makes understanding iron mineralogy within CC meteorites important for understanding both the formation of the Solar System and potentially how life started on Earth. ^{57}Fe Mössbauer spectroscopy is a non-destructive technique that allows for the analysis of iron mineralogy (Gütlich and Schröder, 2012; Yoshida and Langouche, 2013). In this study CC meteorites are analysed by Mössbauer spectroscopy and compared to data from the literature. Here, we present the first Mössbauer spectra for several different meteorite specimens. Studying CC meteorites with Mössbauer Spectroscopy will allow for a further understanding of the role of iron in organic evolution and how terrestrial alteration can affect mineralogy (Bonsall et al., 2022).

6.2. Background

6.2.1. Meteorites

Meteorites are currently defined as extraterrestrial material that falls to Earth (Rubin and Grossman, 2010), however meteorites have been identified on other planetary surfaces, such as on the Martian and Lunar surfaces (Joy et al., 2020; Kah and MSL Science Team, 2015; Schröder et al., 2008). To understand how they relate to each other and to identify potential parent bodies they are classified into groups reflective of their properties (Lipschutz and Schultz, 2014; Weisberg et al., 2006).

6.2.2. Classification

Meteorites are classified by their mineralogy and isotopic abundances, which gives information on how they formed and their parent body's alteration history. Broadly, they are split into 2 groups: differentiated and undifferentiated. Differentiated meteorites come from bodies that have undergone differentiation (separation of core and mantle material) which is part of the planet forming process. These contain the achondrite, iron and stony-iron meteorites, with meteorites from Mars and the Moon belonging in the achondrite group. Undifferentiated

meteorites come from parent bodies that have not undergone differentiation. Undifferentiated meteorites are made up of a group called chondrites which date back to the formation of the Solar System. Chondrites all contain similar minerals, but their proportions allow them to be grouped into: Ordinary, Carbonaceous, Enstatite and Rumuruti (R) and Kakangari (K) chondrites (Figure 6.1; Table 6.1). Carbonaceous chondrites have a chemical composition (Mg/Si) that is similar to the Sun, whilst having a high organic compound and water content, making them the most primitive group of meteorites (Lipschutz and Schultz, 2014; Suttle et al., 2023).

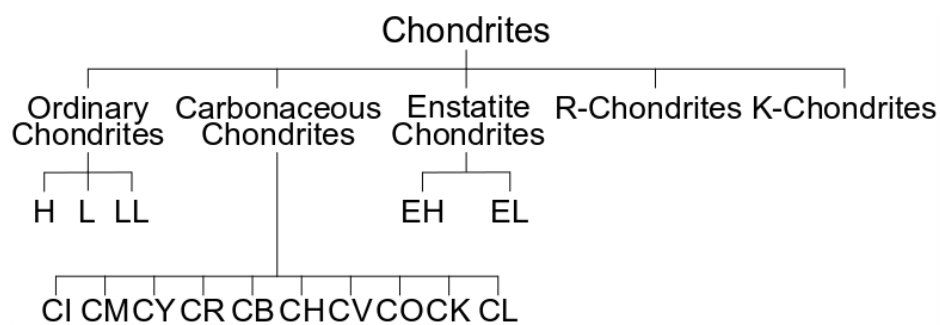


Figure 6.1 - Chondrite group classification (adapted from Lipschutz and Schultz (2014), and Weisberg et al. (2006))

Table 6.1 - Chondrite classification based on chondrule diameter and volume %, Mg/Si ratio, oxidation state and Fe,Ni metal volume % adapted from Weisberg et al., (2006)

Chondrites	Type	Chondrule diameter (mm)	Chondrule (vol%)	Mg/Si Ratio	Oxidation state	Metal (vol%)
Carbonaceous (C)	Ivuna (I)	None	<<1	Solar	Highly oxidised	0
	Mighei (M)	0.30	20	Solar	Highly oxidised	0.1
	Yamato (Y)	Relict	Relict	Solar	Highly oxidised	0.8
	Renazzo (R)	0.70	50-60	Solar	Reduced	5-8
	Bencubbin (B)	10.00 (a) 0.20-1.00 (b)	20-40	Solar	Highly reduced	>50 (a) ~70 (b)
	High-metal (H)	0.02	70	Solar	Highly reduced	~20
	Vigarano (V)	1.00	45	Solar	-	0-5
	Ornans (O)	0.15	48	Solar	-	1-5
	Karoonda (K)	1.00	45	Solar	Highly oxidised	0-5
	Loongana (L)	0.40	~70	Solar	-	3-6
	Ungrouped (ung)	Variable	Variable	Solar	Variable	Variable
	Anomalous (an)	Variable	Variable	Solar	Variable	Variable
	Ordinary	Low-iron, low metal (LL)	0.90	60-80	Sub-solar	Reduced
Low-iron (L)		0.70	60-80	Sub-solar	Reduced	4
High-iron (H)		0.30	60-80	Sub-solar	Reduced	8
Enstatite (E)	Low-iron (L)	0.60	60-80	Sub-solar	Highly reduced	~10

	High-iron (H)	0.20	60-80	Sub-solar	Highly reduced	~10
Rumuruti (R)		0.40	>40	Sub-solar	Highly oxidised	0.1
Kakangari (K)		0.60	27	Sub-solar	Reduced	6-10

Carbonaceous chondrites are further split into groups depending on their mineralogical compositions and how similar they are to others. Groups are based on mineralogical similarities to the well-studied meteorites: Ivuna (CI), Mighei (CM), Yamamoto-82162 or Yamamoto-86720 (CY), Renazzo (CR), Bencubbin (CB), ALH 85085 (CH), Vigarano (CV), Ornans (CO), Karoonda (CK) and Loongana (CL). Meteorites that are unique and do not fit into these groups are listed as ungrouped (ung) or anomalous (an) until they can be placed into a group (either by further research or similar meteorites are found to form a new group). Groups are further divided depending on their

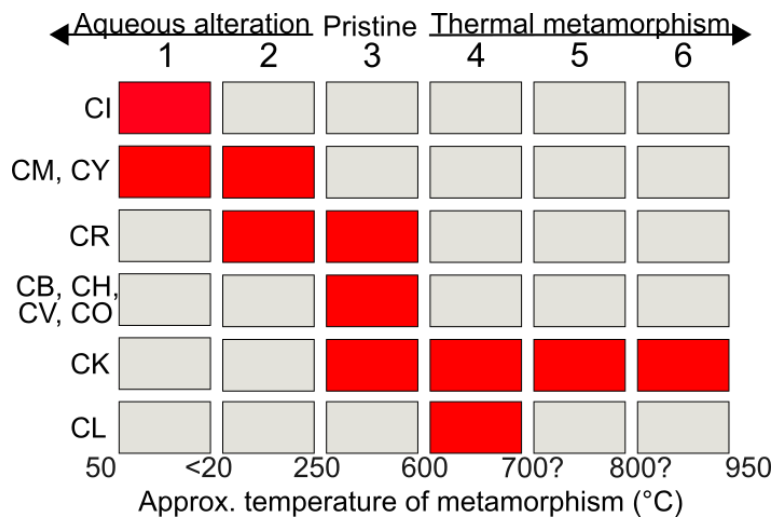


Figure 6.2 - Petrologic groupings of carbonaceous chondrites (adapted from Lipschutz and Schultz (2014), and Weisberg et al. (2006))

level of alteration and labelled numbers 1 through 6, known as the petrologic type (**Error! Reference source not found.**). The level of alteration is inferred from the mineralogy and overall chemistry. From this the approximate temperature and form of alteration can be inferred and usually groups have similar petrologic type, for example all CI chondrites are petrologic type 1, and the CR group is in types 2 and 3 (Figure 6.2) (Weisberg et al., 2006).

The analysis of meteorites with Mössbauer spectroscopy has been carried out not long after the invention of ⁵⁷Fe Mössbauer spectrometers (Yoshida and Langouche, 2013).

Mössbauer spectroscopy has mostly been used to work out levels of terrestrial alteration (Burns et al., 1995; Fisher and Burns, 1991; Sephton et al., 2004) or for reclassification into new groups (Kubuki et al., 2012). This work analysed carbonaceous chondrites yet to be analysed with Mössbauer spectroscopy, Bells, Flensburg and Sutter's Mill, all of which are yet to be grouped. The previously well analysed meteorites, Orgueil and Cold Bokkeveld were also analysed to observe degradation over time due to storage. The other meteorite analysed as part of this project is the Winchcombe meteorite, with the data having been published in the Meteoritics and Planetary Science Journal special issue on said meteorite (Bates et al., 2023).

6.3. Materials and Methods

6.3.1. Fe mineralogy

Published mineralogy from literature of CC meteorite analysis with Mössbauer spectroscopy has been collated to observe how iron mineralogy varies between groups, finds and falls. This is combined with measurements done as part of this study (Section 6.5.2). Along with this, where possible, the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio was calculated to observe the effects of iron oxidation for different petrographic and mineralogical groups along with observing weathering levels of found meteorites compared to falls.

6.3.2. Selection of meteorites specimen for Mössbauer spectroscopy

Meteorites for further Mössbauer spectroscopy analysis were selected on the basis of how they were stored, if they had been analysed with Mössbauer spectroscopy previously, and the length of time it took to retrieve the meteorite after their fall (if known). The intent of this was to expand on the current knowledge of iron mineralogy of carbonaceous chondrites and how much this can tell us about the effects of terrestrial alteration.

Bells Meteorite

The Bells meteorite fell in northeast Texas, USA on the 9th September 1961. 1 fragment was collected the next day after hitting a roof in pristine condition. Other fragments were not collected until after a period of rainfall and a hurricane, but relatively unaltered state (although most shattered either due to impact or weathering) (Monnig, 1963). The Bells meteorite is matrix rich, containing unaltered olivine and similar to the anomalous CR2 meteorite Al Rais, and likely to also be in the same group (Marrocchi et al., 2023). Currently, Bells is still seen as an ungrouped petrologic type 2 meteorite, meaning its undergone very little aqueous alteration (). Fragments of this meteorite were provided by the Natural History Museum, London, UK and analysed with the MIMOS II instrument (Chapter 2) (Table 6.2).

Cold Bokkeveld Meteorite

The Cold Bokkeveld meteorite was an observed fall in South Africa, 1838 (Lee, 1993). Similar to the Winchcombe meteorite, Cold Bokkeveld is a CM2 meteorite so contains small chondrules, refractory inclusions and abundant hydrated minerals with a fine-grained matrix (Weisberg et al., 2006). A fragment of this meteorite was provided by the National Museums Scotland, Edinburgh, UK. The fragment has part of the fusion crust; both the interior and crust were analysed with the MIMOS II instrument (Chapter 2) (Table 6.2).

Flensburg Meteorite

The Flensburg meteorite is a well observed fall across the Netherlands, Germany, Belgium, Denmark and the UK before it was found a day later on the 13th September 2019 in Northern Germany. It is a unique petrologic type 1 meteorite, rich in phyllosilicate, lacking olivine and highly brecciated (Bischoff et al., 2021). It is thought to be similar to the planetesimals that brought the building blocks for water to the Earth's surface during early Solar System History. A thin section of the meteorite was provided by the Institut für Planetologie, University of Münster, Germany, which was analysed with the MIMOS II instrument (Chapter 2) (Table 6.2).

Orgueil Meteorite

The Orgueil meteorite was an observed fall in France, 1884. Orgueil is a carbonaceous chondrite of the CI group and petrographic type 1. To be a carbonaceous chondrite, a meteorite needs to have Mg/Si ratios close to the solar value, with O isotope compositions plotting below terrestrial values (Gounelle and Zolensky, 2014). The CI group is classified by carbonaceous chondrites that lack chondrules and refractory inclusion but have a high degree of hydration much like the Ivuna meteorite which the group is named after (Gounelle and Zolensky, 2014; Weisberg et al., 2006). Petrographic type 1 meteorites have undergone aqueous alteration, with most of the primary minerals being altered and replaced by secondary phases (Gounelle and Zolensky, 2014). A degraded powder sample of this meteorite were provided by the National Museums Scotland, Edinburgh, UK. The powder was analysed at room temperature, 77 and 4.2 K using a Wissel instrument (Chapter 2) (Table 6.2).

Sutters Mill Meteorite

The Sutter's Mill meteorite fell in California, USA on the 22nd April 2012 and was collected a couple of days afterwards. During this time, one fragment of the meteorite was crushed by a car tyre resulting in terrestrial soil adhering to these fragments (Ruzicka et al., 2014). Sutter's Mill is composed of a variety of different CM-like fragments of different petrologic groupings along with fragments from enstatite chondrites and aubrites (Zolensky et al., 2014). This makes placing Sutter's Mill into a specific group challenging so is simply called a carbonaceous (C) chondrite. A thin section from this meteorite was provided by the Natural History Museum, London, UK and analysed with the MIMOS II instrument (Chapter 2) (Table 6.2). A constrained spectrum fit (i.e. doublets and sextets used are only those from known parameters) was used due to the poor signal/noise ratio from a combination of low sample amount and a weak ⁵⁷Co source for the MIMOS II instrument.

6.3.3. Winchcombe Meteorite

The Winchcombe meteorite fell on the 28th February, 2021 in Gloucestershire, UK (McMullan et al., 2024). Following the fall, samples were quickly collected by several members of the public and scientific community, allowing minimal terrestrial alteration to occur. Based on its petrographic and chemical characteristics, the Winchcombe meteorite has been classified as a CM2 chondrite (Bates et al., 2023; McMullan et al., 2024; Suttle et al., 2024). The CM group are classified by having small chondrules and refractory inclusions (0.3 mm), with abundant fine-grained matrix and hydrated minerals like the Mighei meteorite which the group is named after. Petrographic type 2 meteorites are much like the CM group description: abundant hydrated minerals and fine-grained matrix, with chondrules present; they also contain Ni sulfides (Weisberg et al., 2006). Fragments and a powder sample from the meteorite were provided by the Natural History Museum, London, UK. Fragments were analysed with a MIMOS II instrument, whilst the powder was measured at low temperatures with a Wissel instrument (Chapter 2) (Table 6.2).

Table 6.2 - Meteorites studying in this project with their condition, type of Mössbauer spectrometer used and where the meteorite was loaned from

Meteorite	Sample Condition	Mössbauer spectrometer used	On loan from
Bells	Several ~1 cm diameter rock fragments	Backscattering	Natural History Museum, London, UK
Cold Bokkeveld	~5 cm rock fragment	Backscattering	National Museums of Scotland, Edinburgh, UK
Flensburg	Thin Section (~1 cm diameter)	Backscattering	Institut für Planetologie, University of Münster, Germany
Orgueil	Powder* (~100 mg)	Transmission	National Museums of Scotland, Edinburgh, UK
Sutter's Mill	Thin Section (~3 mm diameter)	Backscattering	Natural History Museum, London, UK
Winchcombe	Powder and fragment (See Bates et al. (2023) for sample weights)	Transmission and Backscattering	Natural History Museum, London, UK

*Rock fragments degraded over time

6.4. Results and discussion

6.4.1. Literature results

Currently in the literature, only 70 out of 3144 approved carbonaceous chondrites on Earth (as of 27/05/2024) have been analysed with Mössbauer spectroscopy (Table 6.3; Figure 6.3). Only a fraction of each carbonaceous chondrite group has been analysed with Mössbauer spectroscopy (Figure 6.3), showing potential gaps in knowledge about the iron mineralogy of carbonaceous chondrites.

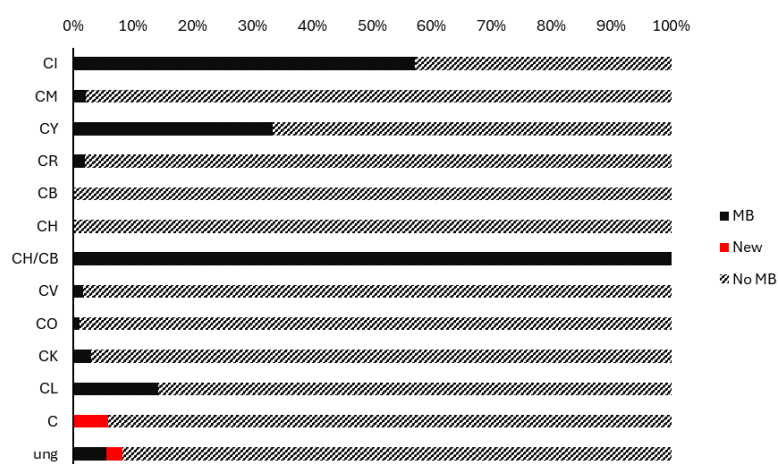


Figure 6.3 - Graph showing the relative percentages of carbonaceous chondrite meteorites analysed with Mössbauer spectroscopy (MB), ones analysed in this study (New) and those that haven't been analysed with Mössbauer spectroscopy (No MB). Data provided in Table 6.3 - Number of carbonaceous chondrite meteorites analysed with Mössbauer spectroscopy (MB), those that have not been analysed with Mössbauer spectroscopy (No MB), numbers analysed in this study (New), and totals of all carbonaceous chondrites on Earth

Table 6.3 - Number of carbonaceous chondrite meteorites analysed with Mössbauer spectroscopy (MB), those that have not been analysed with Mössbauer spectroscopy (No MB), numbers analysed in this study (New), and totals of all carbonaceous chondrites on Earth that belong in the stated groups

Group	MB	No MB	New	Total
CI	4	3	0	7
CM	16	729	0	745
CY	3	6	0	9
CR	4	204	0	208
CB	0	23	0	23
CH	0	28	0	28
CH/CB	1	0	0	1
CV	12	704	0	716
CO	8	744	0	752
CL	17	541	0	558
CK	1	6	0	7
C	0	16	1	17
Ungrouped	4	67	2	73
Totals	70	3070	3	3144

6.4.2. Fe mineralogy

Compiling mineralogy from the literature allows for comparisons to be made between groups and potential terrestrial alteration affecting found meteorites (Table 6.4). Where doublets or sextets aren't identified but are present in the spectra, these have been specified as Unspecified Mössbauer spectroscopy features (Table 6.4). Unidentified Fe²⁺ doublets are likely to be olivine, serpentine or a mixture of the two. Discrepancies appear due to incomplete publishing of Mössbauer spectroscopy results, for example Kubuki et al. (2012) only published that Mössbauer spectroscopy detected magnetite and nothing else. A full publication of minerals detected by Mössbauer spectroscopy in the CK group meteorites would likely also include olivine and a Fe³⁺ doublet (Table 6.4). Mössbauer spectroscopy detected Fe,Ni metal in all analysed CR meteorites (Table 6.4), meaning Fe,Ni metal was likely also detected in Coolidge but not published. A key take-away from this is that only found meteorites such as ALH 83108, Colony, Coolidge and LEW 85332 contain goethite or haematite which is evidence of terrestrial alteration. Goethite forms during periods of aqueous alteration, whilst hematite forms at elevated temperatures in arid conditions from iron oxides of aqueous origin (Cornell and

Schwertmann, 2003). This means that sometime since their fall and subsequent find they underwent aqueous alteration that resulted in the formation of goethite, or in the case of colony, underwent a form of aqueous alteration followed by a drying out period to form hematite. Another mineral of note is the occurrence of maghemite in both Orgueil and Colony (Table 6.4). Maghemite forms due to oxidation of magnetite in both wet or dry conditions (Cornell and Schwertmann, 2003). This likely occurred in Colony during the formation of hematite, whilst Orgueil is a meteorite collected shortly after its fall so hasn't had the time for terrestrial alteration to have an effect. Instead maghemite in the Orgueil sample was likely formed due to improper storage of the sample that caused oxidation over time. Maghemite was detected in several different Orgueil samples from the Muséum national d'Histoire naturelle, Paris, France (Roskosz et al., 2023); Geological Museum, Copenhagen, Denmark (Madsen et al., 1986); and the National Museums of Scotland (this work). (Czakó-Nagy et al., 2003) stated the possibility of the Kaba meteorite also containing maghemite, which also suggests improper storage.

Table 6.4 - Mineralogy of different carbonaceous chondrites analysed with Mössbauer spectroscopy

Class	Petrologic type	Name	Iron oxides					Rock forming minerals			Iron sulfides					Fe-Ni metals				Secondary Minerals					Unspecified Mössbauer spectroscopy feature				Fall or Find	Collection time (days)	References
			Magnetite	Ferrihydrite	Maghemite	Goethite	Haematite	Silicate	Olivine	Pyroxene	Sulfide	Pyrrhotite	Troilite	Pentlandite	FeSONi	Fe,Ni metal	Martensite	Kamacite	Taenite	Serpentine	Cronstedtite	Tochilinite	Clay	Carbonate	Superparamagnetic	Paramagnetic	Fe ³⁺ Doublet	Fe ²⁺ Doublet			
CI	1	Alais	Y	Y			Y	Y		Y	Y											Y		Y	Y		A	0	[1-4]		
CI	1	Orgueil	Y†	Y	Y†		Y	Y†	Y	Y†									Y	Y		Y		Y	Y	Y	A	0	[1-15, †]		
CI	1	Tonk	Y	Y																					Y		A	0	[2]		
CI	1	Ivuna	Y	Y																					Y		A	0	[2]		
CI	1	Ryugu	Y								Y											Y					S	-	[4]		
C	1	ALH						Y																			I	-	[5]		
M		88045																													
C		ALH									Y								Y	Y	Y				Y	Y	I	-	[1, 8, 16, 17]		
M	1/2	83100																													

Class	Petrologic type	Name	Iron oxides					Rock forming minerals			Iron sulfides					Fe-Ni metals				Secondary Minerals					Unspecified Mössbauer spectroscopy feature				Fall or Find	Collection time (days)	References
			Magnetite	Ferrihydrite	Maghemite	Goethite	Haematite	Silicate	Olivine	Pyroxene	Sulfide	Pyrrhotite	Troilite	Pentlandite	FeSONi	Fe,Ni metal	Martensite	Kamacite	Taenite	Serpentine	Cronstedtite	Tochilinite	Clay	Carbonate	Superparamagnetic	Paramagnetic	Fe ³⁺ Doublet	Fe ²⁺ Doublet			
C	2	ALH 82100																							Y		I	-	[18]		
M																															
C	2	Boriskino	Y																							Y	Y	A	0	[19]	
M		o																													
C	2	Cold Bokkeveld	†					Y	†		Y								Y	Y	Y				Y	Y†	Y	A	0	[1, 2, 7, 16, 17, †]	
M																															
C	2	Erakot	Y					Y																		Y	Y		A	0	[1, 18]
M																															
C	2	Kivesväära						Y																		Y	Y	I	-	[1, 18]	
M																															
C	2	LEW 90500									Y									Y	Y					Y	Y	I	-	[16, 17]	
M																															
C	2	Mighei						Y	Y	Y				Y				Y							Y	Y	Y	A	0	[1, 3,	
M																															

Class	Petrologic type	Name	Iron oxides					Rock forming minerals			Iron sulfides					Fe-Ni metals				Secondary Minerals					Unspecified Mössbauer spectroscopy feature					Collection time (days)	References
			Magnetite	Ferrihydrite	Maghemite	Goethite	Haematite	Silicate	Olivine	Pyroxene	Sulfide	Pyrrhotite	Troilite	Pentlandite	FeSONi	Fe,Ni metal	Martensite	Kamacite	Taenite	Serpentine	Cronstedtite	Tochilinite	Clay	Carbonate	Superparamagnetic	Paramagnetic	Fe ³⁺ Doublet	Fe ²⁺ Doublet	Fall or Find		
C M	2	Mukund p-ara																		Y	Y						Y	Y	A	0	[14, 18] [20, 21]
C M	2	Murchison	Y					Y	Y	Y	Y	Y		Y	Y	Y				Y	Y	Y	Y			Y	Y	Y	A	0	[1, 2, 5, 13, 14, 16, 17, 22-26]
C M	2	Murray	Y					Y			Y															Y	Y	Y	A	0	[1, 17, 18]

Class	Petrologic type	Name	Iron oxides					Rock forming minerals			Iron sulfides					Fe-Ni metals				Secondary Minerals					Unspecified Mössbauer spectroscopy feature				Fall or Find	Collection time (days)	References
			Magnetite	Ferrihydrite	Maghemite	Goethite	Haematite	Silicate	Olivine	Pyroxene	Sulfide	Pyrrhotite	Troilite	Pentlandite	FeSONi	Fe,Ni metal	Martensite	Kamacite	Taenite	Serpentine	Cronstedtite	Tochilinite	Clay	Carbonate	Superparamagnetic	Paramagnetic	Fe ³⁺ Doublet	Fe ²⁺ Doublet			
C M	2	Niger	Y										Y												Y	Y	I	-	[25 , 27]		
C M	2	Nogoya						Y											Y						Y		A	0	[3, 18]		
C M	2	Y-791824																							Y		I	-	[18]		
C M	2	Winchom-be	Y																Y	Y	Y						A	0	[28]		
CY	1/2	Y-82162						Y			Y														Y	Y	I	-	[29]		
CY	2	B-7904										Y													Y	Y	I	-	[18 , 30]		
CY	2	Y-86720		Y				Y				Y																I	-	[29]	
C R	2	Renazzo	Y				Y					Y		Y										Y	Y	Y	A	0	[1, 7, 8]		

Class	Petrologic type	Name	Iron oxides					Rock forming minerals			Iron sulfides					Fe-Ni metals				Secondary Minerals					Unspecified Mössbauer spectroscopy feature				Fall or Find	Collection time (days)	References
			Magnetite	Ferrihydrite	Maghemite	Goethite	Haematite	Silicate	Olivine	Pyroxene	Sulfide	Pyrrhotite	Troilite	Pentlandite	FeSONi	Fe,Ni metal	Martensite	Kamacite	Taenite	Serpentine	Cronstedtite	Tochilinite	Clay	Carbonate	Superparamagnetic	Paramagnetic	Fe ³⁺ Doublet	Fe ²⁺ Doublet			
C	2	EET						Y						Y				Y			Y				Y		I	-	[31		
R		87747																												-	]
C	2	EET							Y									Y			Y				Y		I	-	[18		
R		87770																												-	]
C	2	Al Rais	Y					Y				Y		Y										Y			A	0	[1]		
R-an																															
C	3	Isheyev							Y	Y						Y	Y	Y							Y	Y	Y	I	-	[22	
H/C		o																													, 32-
B																															35]
CV	3	Acfer							Y	Y														Y			I	-	[36		
		082																												-	]
CV	3	ALH	Y																								I	-	[37		
		84028																												-	]
CV	3	ALH	Y																								I	-	[37		
		85006																												-	]
CV	3	Allende	Y					Y	Y	Y			Y	Y								Y		Y	Y	Y	A	0	[1,		
																															6-

Class	Petrologic type	Name	Iron oxides					Rock forming minerals			Iron sulfides					Fe-Ni metals				Secondary Minerals					Unspecified Mössbauer spectroscopy feature					Collection time (days)	References
			Magnetite	Ferrihydrite	Maghemite	Goethite	Haematite	Silicate	Olivine	Pyroxene	Sulfide	Pyrrhotite	Troilite	Pentlandite	FeSONi	Fe,Ni metal	Martensite	Kamacite	Taenite	Serpentine	Cronstedtite	Tochilinite	Clay	Carbonate	Superparamagnetic	Paramagnetic	Fe ³⁺ Doublet	Fe ²⁺ Doublet	Fall or Find		
CV	3	Axtell							Y	Y																Y	I	-			8, 14, 36-44] [36, 37]
CV	3	Bali	Y					Y				Y														Y		A	0		[1]
CV	3	Efremovka	Y																									I	-		[37]
CV	3	Grosnaja	Y					Y				Y														Y		A	0		[1, 37]
CV	3	Kaba	Y					Y	Y	Y			Y	Y		Y				Y						Y		A	0		[1, 3, 37, 45]
CV	3	Leoville	Y					Y	Y				Y			Y							Y		Y	Y	I	-			[1, 27,

Class	Petrologic type	Name	Iron oxides					Rock forming minerals			Iron sulfides					Fe-Ni metals				Secondary Minerals					Unspecified Mössbauer spectroscopy feature				Fall or Find	Collection time (days)	References
			Magnetite	Ferrihydrite	Maghemite	Goethite	Haematite	Silicate	Olivine	Pyroxene	Sulfide	Pyrrhotite	Troilite	Pentlandite	FeSONi	Fe,Ni metal	Martensite	Kamacite	Taenite	Serpentine	Cronstedtite	Tochilinite	Clay	Carbonate	Superparamagnetic	Paramagnetic	Fe ³⁺ Doublet	Fe ²⁺ Doublet			
CV	3	Mokoia	Y					Y	Y	Y				Y					Y					Y				A	0	44, 46]	
CV	3	Vigaran o	Y					Y	Y	Y				Y				Y						Y				A	>0	[1, 3, 37]	
C	3	Colony	Y		Y		Y			Y							Y								Y			I	-	[38]	
O	3.2	Kainsaz						Y						Y				Y						Y				A	0	[1]	
O	3.3	Felix						Y						Y				Y						Y				A	0	[1]	
O	3.4	Ornans	Y					Y						Y				Y										A	0	[1]	
O	3.5	Lance						Y						Y				Y						Y				A	0	[1]	

Class	Petrologic type	Name	Iron oxides					Rock forming minerals			Iron sulfides					Fe-Ni metals				Secondary Minerals					Unspecified Mössbauer spectroscopy feature				Fall or Find	Collection time (days)	References
			Magnetite	Ferrihydrite	Maghemite	Goethite	Haematite	Silicate	Olivine	Pyroxene	Sulfide	Pyrrhotite	Troilite	Pentlandite	FeSONi	Fe,Ni metal	Martensite	Kamacite	Taenite	Serpentine	Cronstedtite	Tochilinite	Clay	Carbonate	Superparamagnetic	Paramagnetic	Fe ³⁺ Doublet	Fe ²⁺ Doublet			
C	3.5	ALH				Y									Y													I	-	[8]	
O		83108																													
C	3.7	Warrenton					Y				Y				Y									Y				A	0	[1]	
C	3.8	Isna					Y				Y				Y									Y				I	-	[1]	
O																															
CK	3	PCA	Y																									I	-	[48]	
		82500																													
CK	4	ALH	Y																									I	-	[48]	
		85002																													
CK	4	DAV	Y																									I	-	[48]	
		92300																													
CK	4	EET	Y																									I	-	[48]	
		99430																													
CK	4	LAR	Y																									I	-	[48]	
		04318																													
CK	4	LEW	Y																						Y	Y		I	-	[48]	
		86258																													

Class	Petrologic type	Name	Iron oxides					Rock forming minerals			Iron sulfides					Fe-Ni metals				Secondary Minerals					Unspecified Mössbauer spectroscopy feature				Fall or Find	Collection time (days)	References
			Magnetite	Ferrihydrite	Maghemite	Goethite	Haematite	Silicate	Olivine	Pyroxene	Sulfide	Pyrrhotite	Troilite	Pentlandite	FeSONi	Fe,Ni metal	Martensite	Kamacite	Taenite	Serpentine	Cronstedtite	Tochilinite	Clay	Carbonate	Superparamagnetic	Paramagnetic	Fe ³⁺ Doublet	Fe ²⁺ Doublet			
CK	4	PCA 91470	Y																									I	-	[48]	
CK	4	Karoonda	Y					Y																	Y		A	14	[7]		
CK	5	EET 87526	Y					Y																	Y		I	-	[8]		
CK	5	EET 83311	Y																								I	-	[48]		
CK	5	EET 87507	Y																								I	-	[48]		
CK	5	EET 90015	Y																								I	-	[48]		
CK	5	LAP 03784	Y																								I	-	[48]		
CK	5	LAR 06874	Y																								I	-	[48]		
CK	5	RBT 03522	Y																								I	-	[48]		

Class	Petrologic type	Name	Iron oxides					Rock forming minerals			Iron sulfides					Fe-Ni metals				Secondary Minerals					Unspecified Mössbauer spectroscopy feature				Fall or Find	Collection time (days)	References
			Magnetite	Ferrihydrite	Maghemite	Goethite	Haematite	Silicate	Olivine	Pyroxene	Sulfide	Pyrrhotite	Troilite	Pentlandite	FeSONi	Fe,Ni metal	Martensite	Kamacite	Taenite	Serpentine	Cronstedtite	Tochilinite	Clay	Carbonate	Superparamagnetic	Paramagnetic	Fe ³⁺ Doublet	Fe ²⁺ Doublet			
CK	5/6	EET 87860	Y																									I	-	[48]	
CK	6	LAR 06872	Y																									I	-	[48]	
CL	4	Coolidge				Y			Y	Y							Y											I	-	[7, 8, 49]	
C2 - un g	2	Essebi																							Y			A	0	[18]	
C2 - un g	2	Tagish Lake	Y					Y			Y										Y	Y	Y	Y		Y	Y	A	11	[4-6, 50]	
C2 - un g	2	Bells	†						†																	†		A	18	[†]	

Class	Petrologic type	Name	Iron oxides					Rock forming minerals			Iron sulfides					Fe-Ni metals				Secondary Minerals					Unspecified Mössbauer spectroscopy feature				Fall or Find	Collection time (days)	References
			Magnetite	Ferrihydrite	Maghemite	Goethite	Haematite	Silicate	Olivine	Pyroxene	Sulfide	Pyrrhotite	Troilite	Pentlandite	FeSONi	Fe,Ni metal	Martensite	Kamacite	Taenite	Serpentine	Cronstedtite	Tochilinite	Clay	Carbonate	Superparamagnetic	Paramagnetic	Fe ³⁺ Doublet	Fe ²⁺ Doublet			
C3 - ungroup	3	LEW 85332				Y		Y																				I	-	[8]	
C3 - ungroup	3	Ningqiang	Y						Y				Y													Y		A	0	[44]	
C		Sutter's Mill	†						†				†			†	†		†		†					†	†	A	81	[†]	
C1 - ungroup	1	Flensburg	†								†								†	†	†						A	1	[†]		

Y - Mineral found in the meteorite; A - Fall; I - Find; S - Sample return; † - this work;

[1] Bland et al., 2008; [2] Burns and Fisher, 1991; [3] Herr and Skerra, 1968; [4] Roskosz et al., 2023; [5] Bland et al., 2002; [6] Bland et al., 2004; [7] Burns and Fisher, 1990; [8] Fisher and Burns, 1991; [9] Kerridge, 1976; [10] Knudsen, 1989; [11] Madsen et al., 1986; [12] Madsen et al., 1989; [13] Madsen et al., 1995; [14] Roy-Poulsen et al., 1981; [15] Virgo, 1972; [16] Burns and Fisher, 1994; [17] Fisher and Burns, 1993; [18] Sephton et al.,

2004; [19] Malysheva et al., 1981; [20] Tripathi et al., 2018; [21] Dixit et al., 2019; [22] Oshtrakh et al., 2007; [23] Costa et al., 1998; [24] Madsen et al., 1988; [25] Morris et al., 1994; [26] Thompson et al., 2020; [27] Scorzelli et al., 1988; [28] Bates et al., 2023; [29] Scorzelli et al., 1994; [30] Scorzelli and Souza Azevedo, 1994; [31] Burns et al., 1995; [32] Goryunov et al., 2023; [33] Goryunov and Oshtrakh, 2024; [34] Grokhovsky et al., 2009; [35] Oshtrakh et al., 2008; [36] Bland et al., 1995; [37] Bland et al., 2000; [38] Hoffman et al., 2000a; [39] Burns, 1993; [40] Hoffman et al., 2000b; [41] Housley, 1981; [42] Ludwig et al., 2001; [43] Oliver et al., 1984; [44] Shi et al., 1988; [45] Czakó-Nagy et al., 2003; [46] Oliver, 1978; [47] Bland et al., 1997; [48] Kubuki et al., 2012; [49] Elewa and Cadogan, 2017; [50] Baker et al., 2001

Evidence of oxidation within the sample is important to note as if magnetite has been oxidised, then other constituents of the meteorite might also have been, for example organic matter. Kaba fell in 1857 and Orgueil fell in 1864, before proper meteorite storage was considered and implemented meaning more recent falls are less likely to be affected by this. The proper storage of meteorites is important to preserve the original mineralogy. Here we see Mössbauer spectroscopy is a powerful method to identify any alteration to the meteoritical material without causing further damage to the material and highlights the importance of fully publishing results to see evidence of any mineralogical change.

6.4.3. Fe^{3+}/Fe_{tot}

Fe^{3+}/Fe_{tot} is a measurement of how oxidised the iron mineralogy is. Being able to compare the oxidation between finds, fall and sample return allows for insight into how iron mineralogy can change during transit to the Earth's surface and subsequent alteration on the surface. Comparing the results allows to see the variation between petrologic types, groups, falls, finds and sample return (Table 6.5; Figure 6.4). Results from literature and this work are included where possible: for example, not all literature reported mineral percentages; or in the case of Sutter's Mill from this work, the spectrum had too great a signal to noise ratio to quantify, relative percentages accurately.

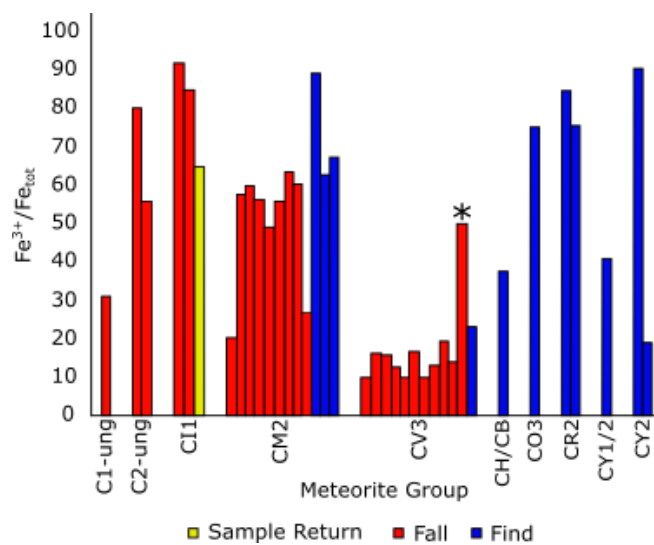


Figure 6.4 - Fe^{3+}/Fe_{tot} ratios for various meteorite finds, falls and sample return. *Underwent HF and HCl treatments before analysis (Housley et al., 1981)

Within the CI1 group, we see an increased ratio in fallen meteorites compared to the sample return from Ryugu (Figure 6.4) by over 20% (Table 6.5), showing that asteroidal material undergoes oxidation during transit to the Earth's surface, likely during the descent through the atmosphere. This is directly observed with Cold Bokkeveld's fusion crust having an Fe^{3+}/Fe_{tot} ratio value of 65.1 compared to the interior value of 20.2 (Section 0), and again with Isheyevo with an interior Fe^{3+}/Fe_{tot} ratio of 37.5 whilst the fusion crust has a value of 64.3 (Oshtrakh et al., 2007). This confirms that only the exterior of the meteorite is altered during the descent to Earth.

The found carbonaceous chondrites are more oxidised than the fall meteorites (Table 6.5; Figure 6.4), which is to be expected as they are exposed to the elements (i.e. rain) for longer.

Table 6.5 - $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ meteorite interior ratio averages for each meteorite group with standard deviations in brackets after value. (Results from Housely et al., (1981) excluded from statistics.)

$\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio value(standard deviation)			
Meteorite Group	Find	Fall	Sample Return
CI1		88.37(3.6)	63.52(0.0)
CM2	72.93(11.4)	50.00(14.7)	
CY1/2	40.65(0.0)		
CY2	54.43(35.8)		
CR2	79.94(4.5)		
CH/CB	37.50(0.0)		
CV3	23.00(0.0)	13.84(10.8)	
CO3	75.00(0.0)		
C1-ung		30.99(0.0)	
C2-ung		68.19(12.1)	

Between the grouped meteorites, a trend from petrographic groups is seen for the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ values. For example, within the falls, CI1 are the most oxidised (88.37) whilst CV3 are the least oxidised (13.84) (Table 6.5). The $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio follows the trend of increasing aqueous alteration from groups 3 to 1 (Figure 6.4), whereas this is not seen for the found meteorites, for example CV3 are the most reduced, whilst CO3 are the most oxidised (Figure 6.4; Table 6.5). The reason for this is likely to be due to the lack of published data for Mössbauer spectroscopy analysis of carbonaceous chondrites preventing full understanding of the oxidation states of the carbonaceous chondrites. Full Mössbauer spectra reporting is needed for meteorites to allow for better comparisons between the oxidation states of fall vs found meteorites. Where

possible, fall meteorites have a lower $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio when compared to the found meteorites in the same group, for example fall CM2=50.00, whilst found CM2=72.93 (Table 6.5). This shows the importance of rapid collection of meteoritical material post-fall to prevent terrestrial alteration causing oxidation to the meteorite.

6.5.2. Mössbauer spectra

Bells

A room temperature backscatter Mössbauer spectrum of the Bells meteorite reveals a mineralogy dominated by magnetite, olivine and a Fe^{3+} phase (Figure 6.5; Table 6.6). The expected ratio for $\text{Fe}^{2.5+}/\text{Fe}^{3+}$ is ~ 2 in magnetite (Yoshida and Langouche, 2013). For the Bells meteorite, the $\text{Fe}^{2.5+}/\text{Fe}^{3+}$ is 1.18, suggesting a larger amount of Fe^{3+} incorporated into the magnetite structure than expected, meaning it is oxidised. The $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ value of Bells is 56.09, making it slightly more oxidised than the average meteorite fall of the same petrologic type (CM2). This higher oxidation level could be due to terrestrial alteration not observed before or due to the features of the parent body undergoing a different process to those of the CM2 parent body resulting in this difference and why Bells is an ungrouped meteorite.

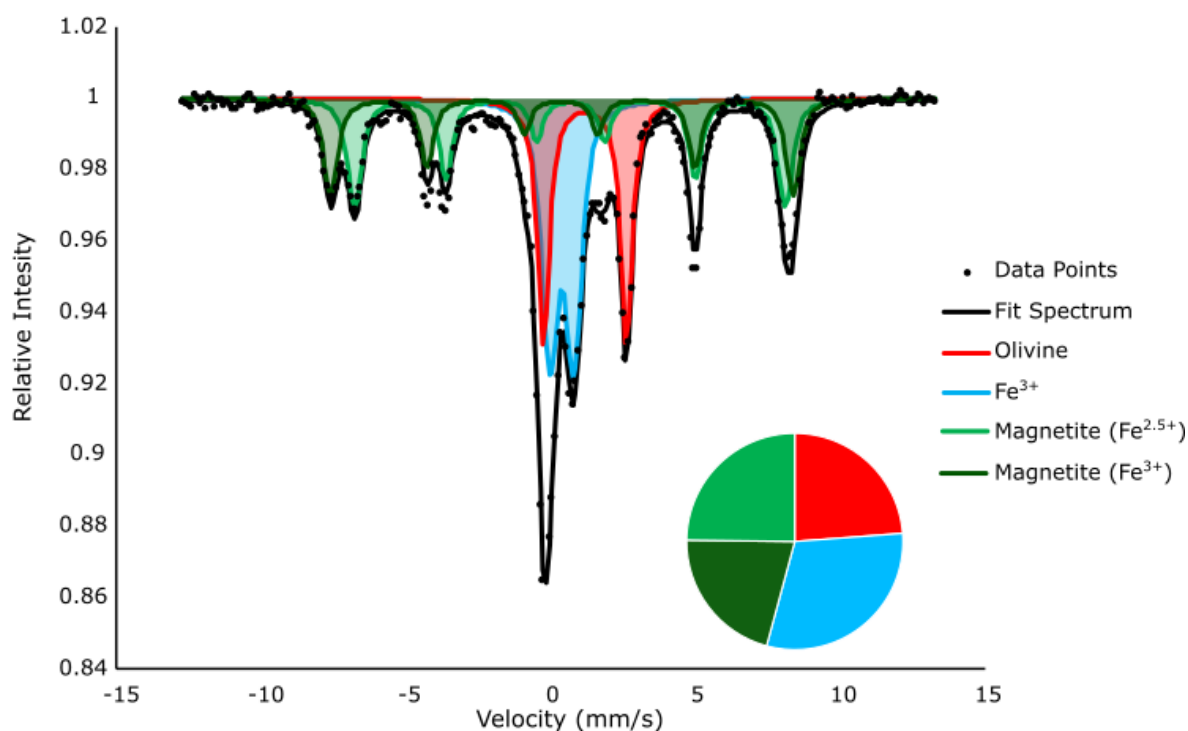


Figure 6.5 - Backscatter Mössbauer spectra of the Bells meteorite at room temperature with a pie chart showing percentage of minerals identified

Table 6.6 - Mössbauer spectrum parameters of the Bells meteorite

Phase	δ (mm/s)	Δ or ϵ (mm/s)	B_{hf} (T)	Area (%)
Olivine	1.14	2.84	-	23.8
Fe ³⁺	0.36	0.83	-	30.4
Magnetite (Fe ^{2.5+})	0.64	-0.01	45.6	24.8
Magnetite (Fe ³⁺)	0.34	0.02	49.0	21.0

Cold Bokkeveld

Room temperature backscatter Mössbauer spectra show the difference between the interior of a meteorite versus the fusion crust (Figure 6.6). The fusion crust has an Fe²⁺ doublet with a lower quadrupole shift ($\Delta = 2.45$ mm/s) (Table 6.8) than what is observed for olivine for the interior spectrum ($\Delta = 2.88$ mm/s) (Table 6.9) but have similar isomer shift (fusion crust $\delta = 1.11$ mm/s (Table 6.8); interior $\delta = 1.14$ mm/s (Table 6.9)), suggesting oxidation of olivine sometime during the descent to the Earth's surface and subsequent collection. A loss of magnetite is seen in the fusion crust (Figure 6.6), which is likely due to oxidation, which resulted in the formation of an amorphous Fe³⁺ phase and is evident with the increased area of the Fe³⁺ doublet in the fusion crust spectrum (Figure 6.6) resulting in a Fe³⁺/Fe_{tot} value of 65.1% compared to the interior value of 20.2%. The Fe³⁺ doublet is likely to be a combination of both cronstedtite and tochilinite, which have been observed within this meteorite with low temperature Mössbauer spectroscopy (Burns and Fisher, 1990, 1991, 1994). Magnetite has a Fe^{2.5+}/Fe³⁺ ratio of 1.93, meaning it is not oxidised (Yoshida and Langouche, 2013), likely protected from oxidation by being in the interior of the meteorite.

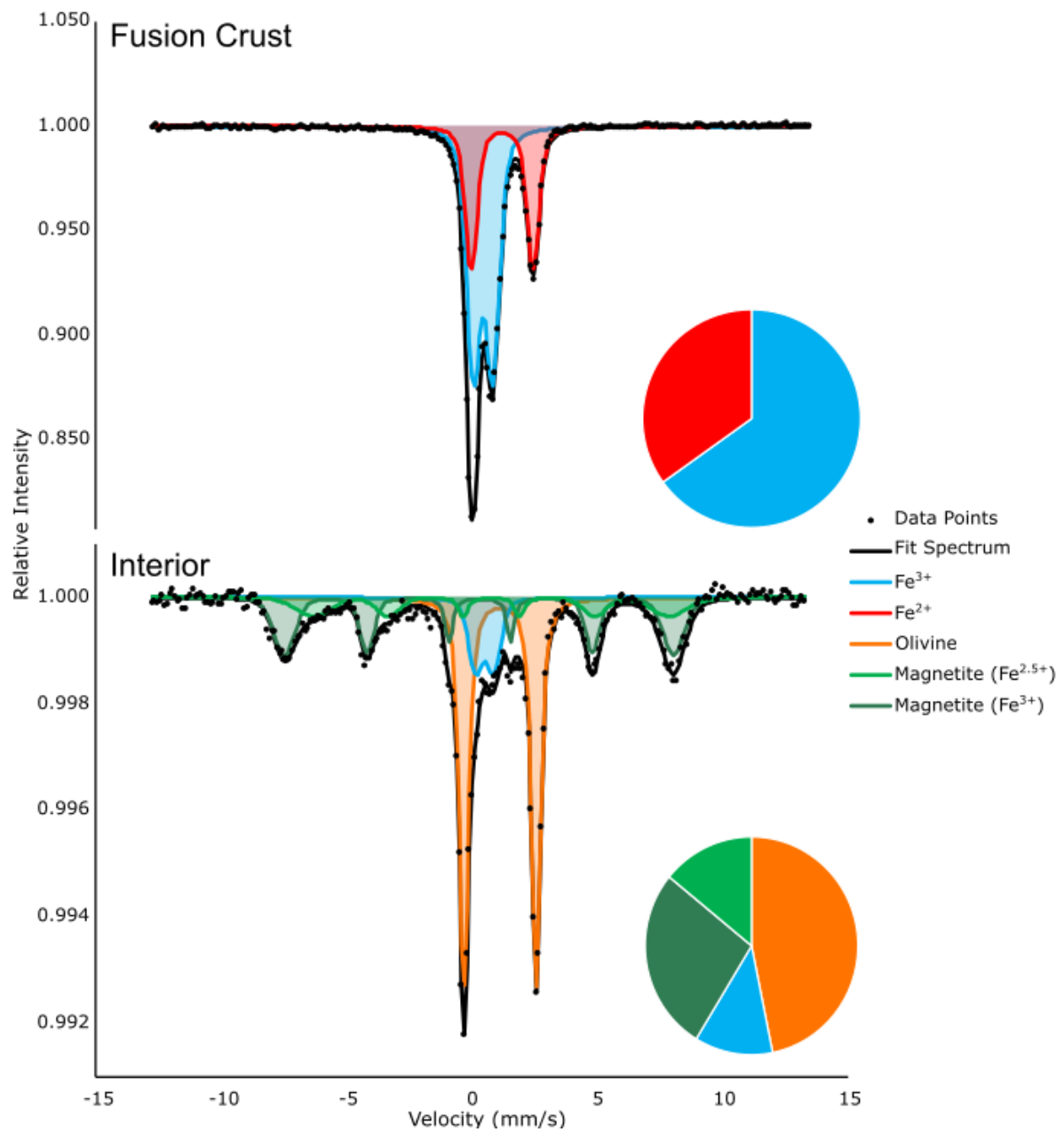


Figure 6.6 - Backscatter Mössbauer spectra of the fusion crust and interior of the Cold Bokkeveld meteorite at room temperature with pie charts showing percentages of minerals identified

Table 6.7 - Mössbauer spectrum parameters of the fusion crust from the Cold Bokkeveld meteorite at room temperature

Phase	δ (mm/s)	Δ or ϵ (mm/s)	B_{hf} (T)	Area %
Fe ³⁺	0.37	0.78	-	65.1
Fe ²⁺	1.11	2.45	-	34.9

Table 6.8 - Mössbauer spectrum parameters of the interior of the Cold Bokkeveld meteorite at room temperature

Phase	δ (mm/s)	Δ or ϵ (mm/s)	B_{hf} (T)	Area %
Fe ³⁺	0.53	0.74	-	11.8
Olivine	1.14	2.88	-	46.5
Magnetite (Fe ^{2.5+})	0.32	-0.01	48.1	27
Magnetite (Fe ³⁺)	0.80	0.00	44.0	14

Flensburg

A room temperature backscatter Mössbauer spectrum of a thin section of the Flensburg meteorite shows a varied iron mineralogy. Like many other CC meteorites analysed with Mössbauer spectroscopy, the Flensburg meteorite contains magnetite, serpentine group minerals (cronstedtite, serpentine) and sulphides (tochilinite, FeS) (Figure 6.7; Table 6.9). The occurrence of serpentine group minerals and iron sulphides suggests a high degree of aqueous alteration resulting in the petrologic group 1 classification. The lack of Fe, Ni metal and transformation of olivine to serpentine again shows the highly aqueously altered nature of the Flensburg meteorite. This aqueous alteration is reflected by a reduced Fe³⁺/Fe_{tot} ratio of 31.0%, suggesting a removal of Fe³⁺ from the mineral matrix. Contrary to this, magnetite has an oxidised Fe^{2.5+}/Fe³⁺ ratio of 0.46, suggesting formation from the aqueous alteration fluid. Another possibility is that the magnetite came from a different parent body that collided with the Flensburg parent body. The highly brecciated nature of Flensburg suggests this is a possibility (Bischoff et al., 2021).

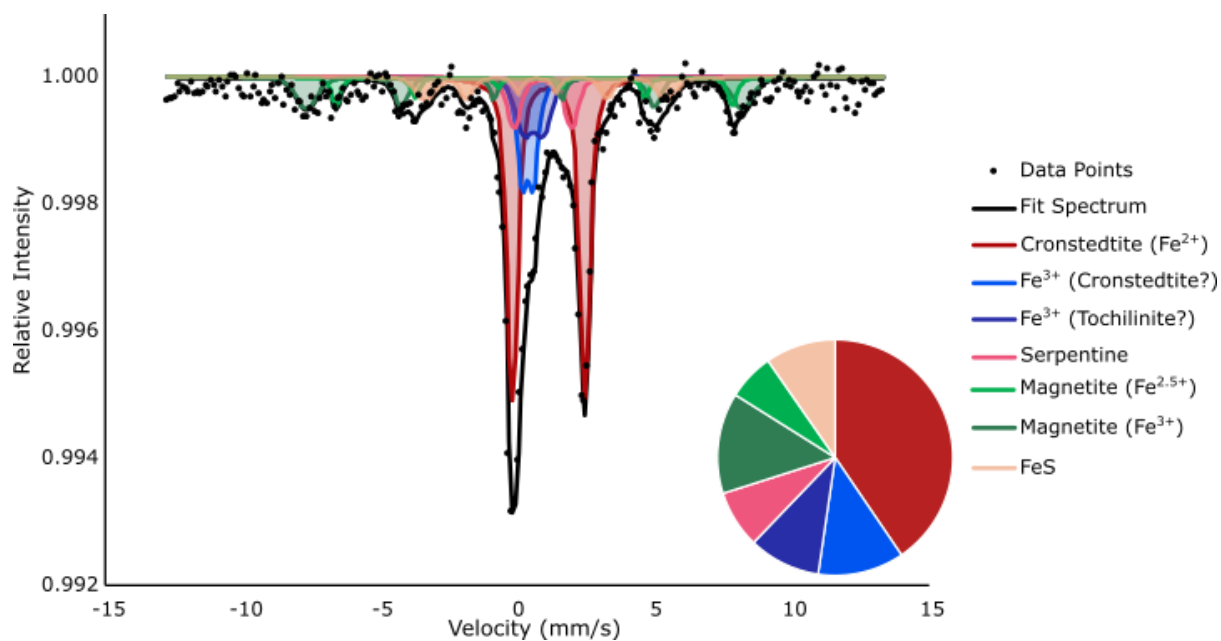


Figure 6.7 - Backscatter Mössbauer spectrum of a thin section of the Flensburg meteorite at room temperature with a pie chart showing percentages of minerals identified

Table 6.9 - Mössbauer spectrum parameters of a thin section of the Flensburg meteorite at room temperature

	δ	Δ	B_{hf}	Area %
Cronstedtite (Fe^{2+})	1.14	2.63	-	41
Cronstedtite (Fe^{3+})	0.38	0.42	-	12
Tochilinite	0.59	0.73	-	10
Serpentine	0.92	2.09	-	8
Magnetite (Fe^{3+})	0.32	-0.06	49.1	14
Magnetite ($Fe^{2.5+}$)	0.53	0.08	44.7	6.5
FeS	0.87	0.16	27.2	9.8

Orgueil

Transmission Mössbauer spectroscopy conducted at room temperature (RT), 77 K and 4.2 K show the iron mineralogy of the Orgueil meteorite for not only well-crystalline phases, but also poorly crystallised (Figure 6.8; Table 6.10). The most predominant mineral identified is maghemite as both a doublet and a sextet (Figure 6.8). The maghemite sextet becomes more prominent as the temperature is decreased, suggesting that the maghemite is poorly crystalline. Maghemite forms from the oxidation of magnetite (Cornell and Schwertmann, 2003), suggesting some form of terrestrial alteration. The background phase is an unknown phase with no similar parameters for a singular mineral, suggesting a mixture of minerals with similar parameters that cannot be separated, resulting in an unidentifiable sextet. The $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ value is 84.7% which reflects the highly oxidised nature of the sample with the occurrence of maghemite.

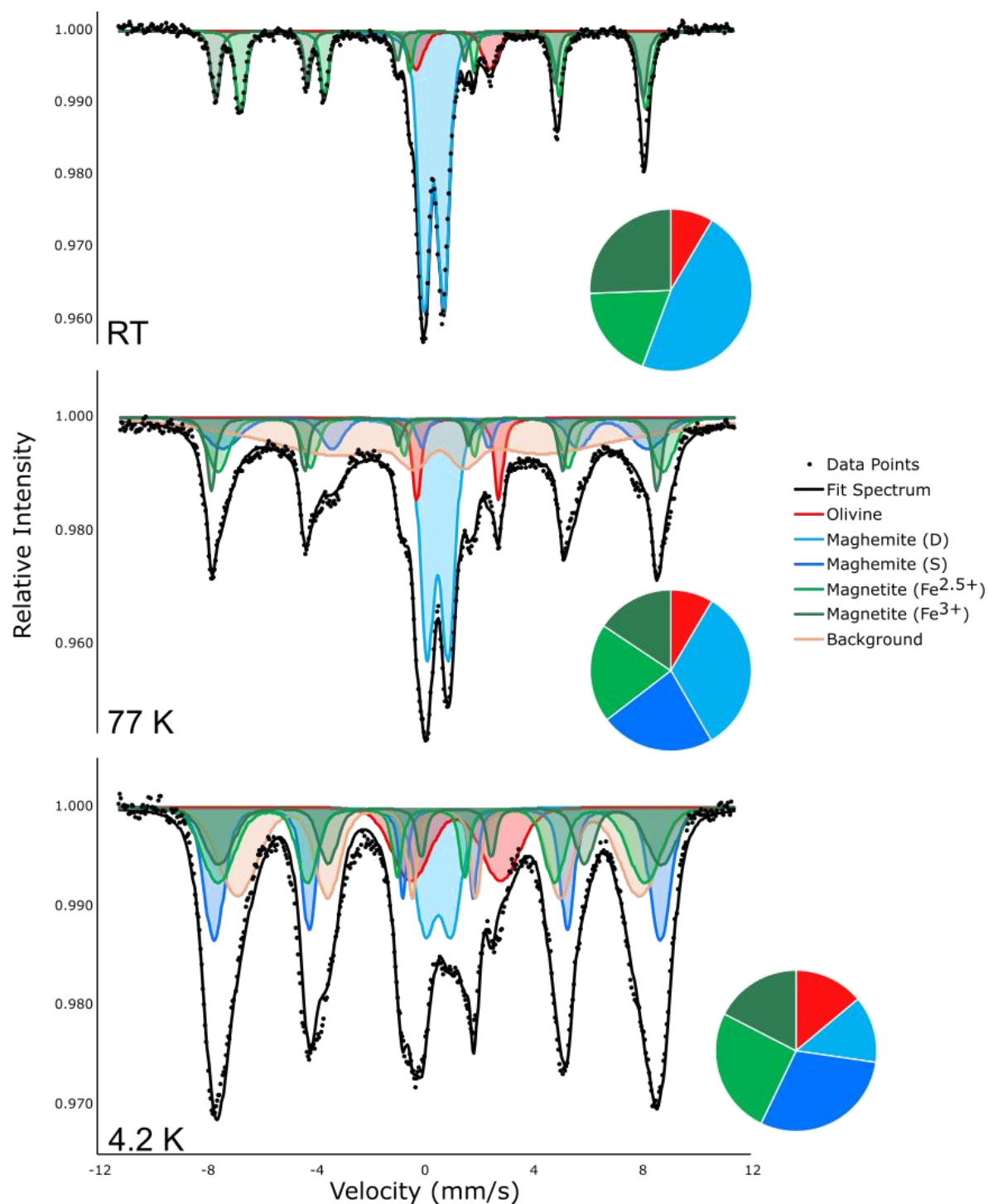


Figure 6.8 - Transmission Mössbauer spectra of a powdered sample of the Orgueil meteorite at room temperature (RT), 77 K and 4.2 K with pie charts showing percentages of minerals identified

Table 6.10 - Mössbauer spectra parameters of the Orgueil meteorite

Temperature	Phase	δ (mm/s)	Δ or ϵ (mm/s)	B_{hf} (T)	Area %
Room Temperature	Olivine	1.07	2.73	-	8.5
	Maghemite (D)	0.37	0.72	-	47.2
	Magnetite (Fe ^{2.5+})	0.24	-0.03	48.7	18.7
	Magnetite (Fe ³⁺)	0.69	0.03	46.1	25.6
77 K	Olivine	1.22	3.01	-	5.5
	Maghemite (D)	0.49	0.78	-	21.4
	Maghemite (S)	0.57	0.03	50.7	14.8
	Magnetite (Fe ^{2.5+})	0.77	-0.36	48.4	12.8
	Magnetite (Fe ³⁺)	0.35	0.01	50.7	10.1
	Background	0.70	0.15	35.6	35.4
4.2 K	Olivine	1.16	3.30	-	10.3
	Maghemite (D)	0.52	0.99	-	9.9
	Maghemite (S)	0.50	-0.02	50.8	22.1
	Magnetite (Fe ^{2.5+})	0.26	0.01	48.6	18.8
	Magnetite (Fe ³⁺)	0.88	-0.30	50.4	12.9
	Background	0.62	-0.10	45.7	26.1

Sutter's Mill

The room temperature backscatter Mössbauer spectrum of Sutter's Mill has a high signal/noise ratio resulting in a poor spectrum (Figure 6.9; Table 6.11). The high signal/noise ratio is likely due to the lack of material within the thin section of the meteorite. To identify potential iron phases, a constrained fit was used where parameters used are only those published in the literature and are not allowed to be altered (Table 6.11). From this constrained fit, we can see a potential mix

of olivine, Fe,Ni metals, Fe sulphides and magnetite (Figure 6.9; Table 6.11). This is in line with what is reported by (Zolensky et al., 2014) from backscatter electron microscopy and electron microprobe analysis. $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ and $\text{Fe}^{2.5+}/\text{Fe}^{3+}$ of magnetite is not calculated for this meteorite due to the uncertainty of the spectrum fit.

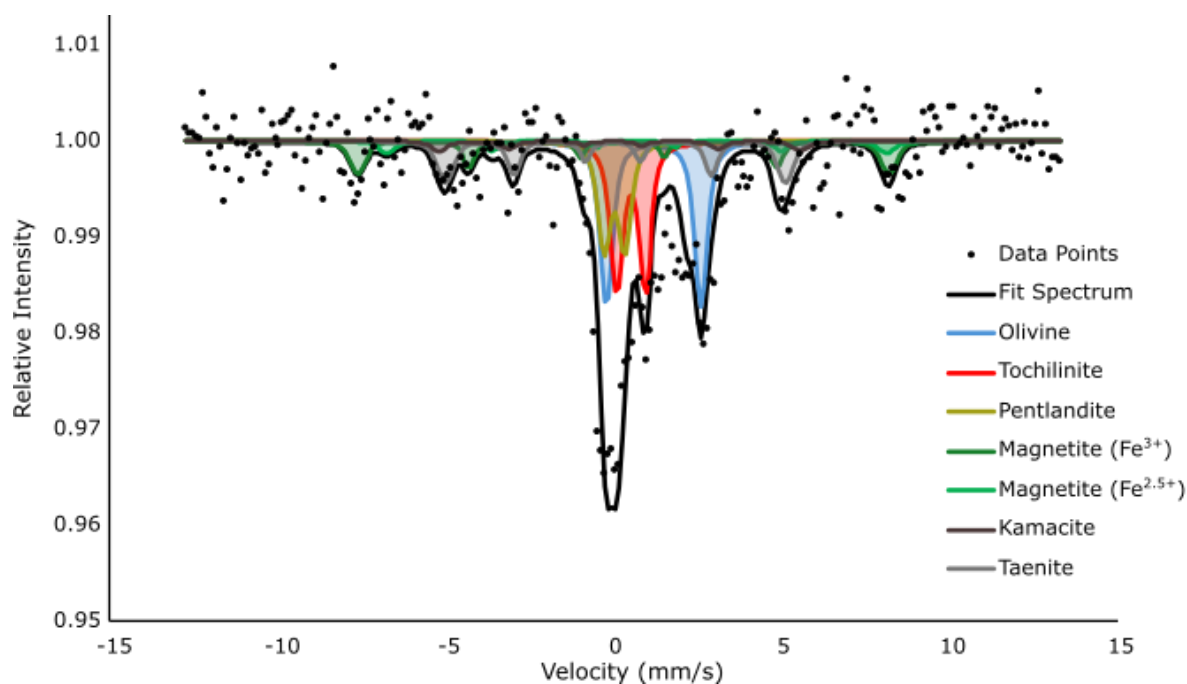


Figure 6.9 - Backscatter Mössbauer spectrum of a thin section of the Sutter's Mill meteorite at room temperature

Table 6.11 - Mössbauer spectrum parameters of a thin section of the Sutter's Mill meteorite at room temperature

Phase	Δ (mm/s)	Δ or ϵ (mm/s)	B_{hf} (T)	Area (%)
Olivine ^a	1.17	2.81		22.9
Tochilinite ^b	0.49	0.85	-	20.5
Pentlandite ^a	0.00	0.60	-	14.7
Serpentine ^b	1.11	2.10	-	10.1
Magnetite ($\text{Fe}^{2.5+}$) ^b	0.67	0.00	46.0	4.0
Magnetite (Fe^{3+}) ^b	0.26	0.00	49.0	10.8
Kamacite ^c	0.06	0.09	33.3	3.3
Taenite ^c	-0.01	0.04	31.4	13.8

^aYoshida and langouche 2012, ^bBates et al 2023, ^cOstrakh et al 2007

Winchcombe

Backscatter Mössbauer spectroscopy was conducted at room temperature on 3 different rock chip samples of the meteorite (Figure 6.10; Table 6.12; Table 6.13), whilst a powder of the meteorite was analysed by transmission Mössbauer spectroscopy at room temperature, 77 K and 4.2 K (Figure 6.11; Table 6.13; Table 6.14). Analysis found the Winchcombe meteorite to contain serpentine group minerals such as serpentine and cronstedtite, Fe sulphides, and magnetite. At 4.2 K, the spectrum is dominated by cronstedtite which is also seen at low temperature measurements of other CM class meteorites like ALH83100 (Fisher and Burns, 1991), Cold Bokkeveld (Burns and Fisher, 1990; 1991), and Mukundpara (Dixit et al 2019). The average $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ value of the Winchcombe meteorite is 27.0%, which is one of the lowest out of CM2 class meteorites. There are two potential reasons for this:

1. Other authors included tochilinite as a ferric paramagnetic phase, whereas here it is not, resulting in the lower $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ than the literature (Bates et al., 2023).
2. Rapid collection of the Winchcombe meteorite post-fall prevented oxidation of iron mineralogy.

By including tochilinite in the ferric phase of the average $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio for Winchcombe, we get a value of 50.1% which is closer in value to the literature values for other fallen CM2 meteorites. This highlights the importance of identifying tochilinite within the meteorite mineralogy to gain a more accurate understanding of the oxidation states.

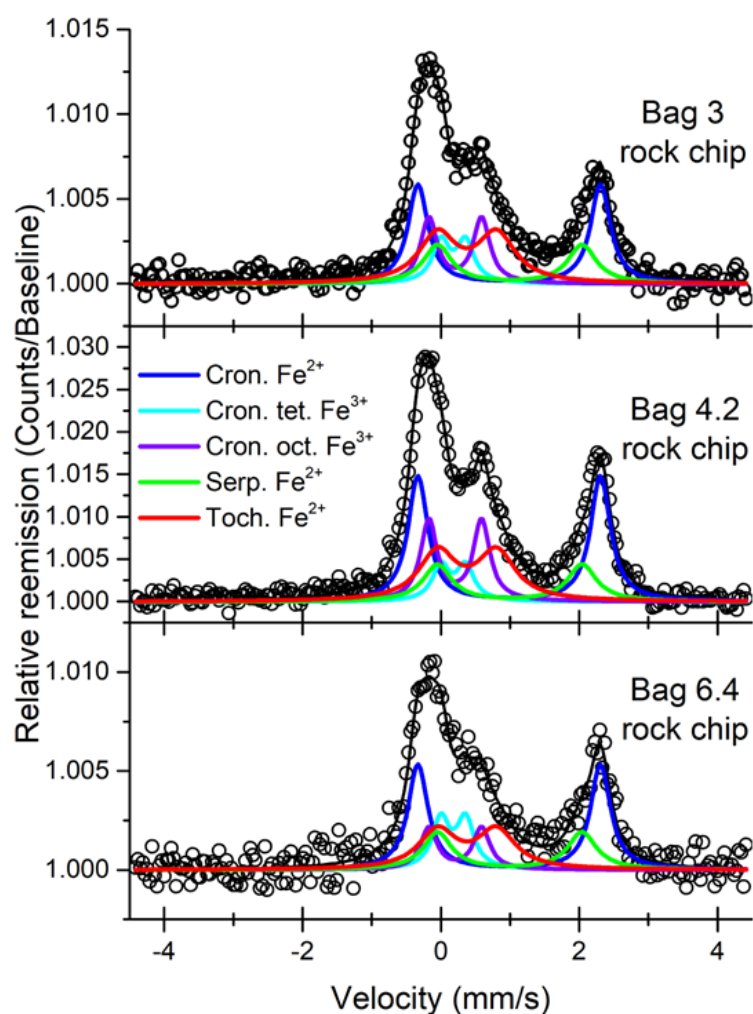


Figure 6.10 - Backscatter Mössbauer spectra of three rock chips of the Winchcombe meteorite obtained at room temperature with the miniaturized Mössbauer spectrometer MIMOS II over a reduced velocity range. Black solid line represents the overall fit to the measured (black open circles) and is the sum of all subspectra (coloured lines). Cronstedtite (Cron.) contains Fe^{2+} and Fe^{3+} , the latter in tetrahedral (tet.) and octahedral (oct.) coordination. Serpentine (Serp.) and tochilinite (Toch.) contain Fe^{2+} (Figure from Bates et al., 2023).

Table 6.12 - Mössbauer spectrum parameters of the Winchcombe meteorite for both transmission and backscattering modes at room temperature (Adapted from Bates et al., 2023)

Phase	δ (mm/s)	Δ or ϵ (mm/s)	B_{hf} (T)
Cronstedtite (Fe^{2+})	1.10	2.64	-
Cronstedtite (Fe^{3+} tetrahedral)	0.29	0.36	-
Cronstedtite (Fe^{3+} octahedral)	0.32	0.76	-
Serpentine	1.11	2.09	-
Tochilinite	0.49	0.85	-

Magnetite (Fe ^{2.5+})	0.26	0.01	49
Magnetite (Fe ³⁺)	0.67	0.00	46

Table 6.13 - percentages of minerals identified by Mössbauer spectroscopy in different samples of the Winchcombe meteorite

Sample	Cronst. Fe ²⁺	Cronst. tet. Fe ³⁺	Cronst. oct. Fe ³⁺	Serp. Fe ²⁺	Toch. Fe ²⁺	Magn. Fe ^{2.5+}	Magn. Fe ³⁺	Fe ³⁺ /Fe ^T
Bag 3 rock chip	29.6	10.6	16.1	16.7	27.1	<lod	<lod	0.27
Bag 4.2 rock chip	34.2	8.2	18.2	14.6	24.8	<lod	<lod	0.26
Bag 4.4 powder	30	9	19	23	17	2	1	0.30
Bag 6.4 rock chip	34	13.7	11.2	17.5	23.5	<lod	<lod	0.25

<lod = below limit of detection

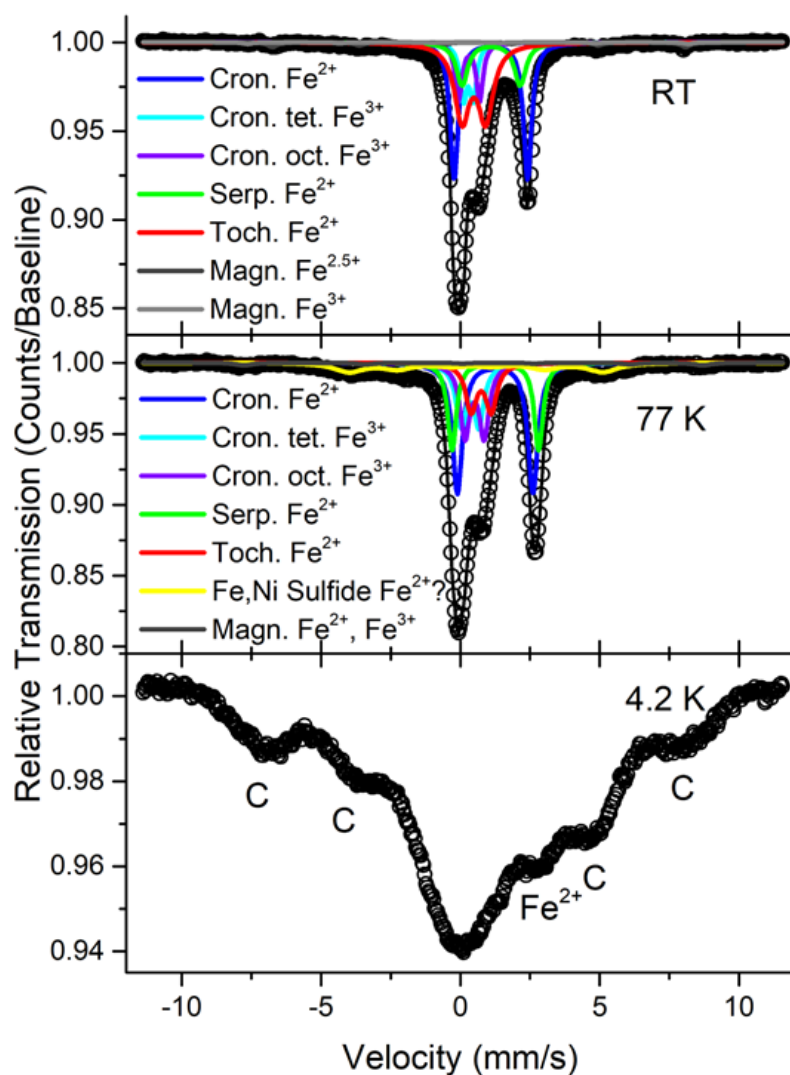


Figure 6.11 - Temperature-dependent Mössbauer spectra of the powdered sample BM.2022,M3-4. Spectra were measured in transmission mode at room temperature (RT), 77, and 4.2 K. The black solid line represents the overall fit to the measured spectrum (black open circles) and is the sum of all subspectra (coloured lines). Cronstedtite (Cron.) contains Fe^{2+} and Fe^{3+} , the latter in tetrahedral (tet.) and octahedral (oct.) coordination. Serpentine (Serp.) and tochilinite (Toch.) contain Fe^{2+} (Figure from Bates et al., 2023).

Table 6.14 - Transmission Mössbauer spectrum parameters of the Winchcombe meteorite at 77 K (Adapted from Bates et al., 2023)

Mineral phase	δ (mm/s)	Δ or ε (mm/s)	B_{hf} (T)	Area (%)
Cronstedtite (Fe^{2+})	1.25	2.72	-	29
Cronstedtite (Fe^{3+} tetrahedral)	0.35	0.64	-	14
Cronstedtite (Fe^{3+} octahedral)	0.51	0.69	-	16
Serpentine	1.26	3.12	-	17
Tochilinite	0.75	0.72	-	12
Fe,Ni sulfide	0.47	0.09	28.3	12
Magnetite (Fe^{2+} , Fe^{3+})	0.91	-0.45	2.0	2

6.5.3. Future Work

To fully comprehend the use of Mössbauer spectroscopy for understanding carbonaceous chondrite mineralogy, more carbonaceous chondrites need to be analysed. Particular focus needs to be given to both CB and CH group carbonaceous chondrites of which none have been analysed with Mössbauer spectroscopy, except for Isheyevo which is a mixture of the two groups. Both CB and CH groups are high in metal (**Error! Reference source not found.**) making them excellent candidates for analysis with Mössbauer spectroscopy which can identify the different metallic iron phases. Mössbauer spectroscopy also potentially has the ability to help group ungrouped meteorites or reclassify them into new groups (Kubuki et al., 2012), however this is a difficult endeavour and not possible within this study due to the incomplete reporting of Mössbauer spectra in the literature. This needs to be addressed in the future to understand the full potential of analysing carbonaceous chondrites with Mössbauer spectroscopy.

6.6. Conclusion

To summarise, Mössbauer spectroscopy measurements have been carried out on meteorites that have either: been poorly stored, not analysed with Mössbauer spectroscopy before or freshly fallen. Using the Mössbauer spectroscopy measurements from the literature and those completed in this project, the oxidation states of the iron mineralogy is known and can be compared where possible. Improper storage can lead to the oxidation of magnetite to maghemite whilst terrestrial alteration can cause the formation of goethite and haematite within the meteorites. This change in mineralogy can potentially also reflect a change in organic composition, which is of particular note due to the apparent association between organic matter and iron minerals in carbonaceous chondrites (Amri et al., 2005; Noun et al., 2019),

however still needs to be studied. The investigation of iron mineralogy and its association with organic matter is important for understanding the evolution of both the solar system and life on Earth.

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7. Discussion

7.1. Overview of Key Results

This research set out to determine how reactive iron species can be identified using different analytical techniques, with the broader goal of understanding their role in the preservation of organic matter under conditions relevant to Mars. By using a combination of terrestrial analogue materials, carbonaceous chondrites, and results from the Martian surface, the study assessed the relative strengths and weaknesses of each technique, providing valuable context for future Mars exploration and sample return missions.

Across the results chapters, several significant findings emerged:

- Detection of nanophase iron oxides and Fe–sulphides in both analogue and meteoritic samples, revealing the prevalence of reactive iron species in a range of geological contexts.
- Instrument-specific detection differences, with Mössbauer spectroscopy proving highly effective in identifying iron mineralogy, XRD excelling at resolving crystalline phases, and Raman spectroscopy detecting organics when fluorescence interference was minimal.
- Sequential extraction results demonstrating complex patterns of iron phase reactivity and, in certain cases, correlated changes in organic carbon content, suggesting that some reactive phases may influence organic matter preservation.
- Particular strength of Mössbauer spectroscopy in analysing the iron mineralogy of carbonaceous chondrites, with minimal destruction to the sample.

Collectively, these results highlight the necessity of integrating multiple methods when characterising iron mineralogy and evaluating its relationship to organic matter on Mars and in meteorites.

7.2. Cross-Chapter Analysis of Results

The findings emphasise the value of combining analytical techniques to achieve a comprehensive characterisation of both crystalline and amorphous iron phases. The complementary nature of Mössbauer spectroscopy and XRD was especially clear: together, they provided a fuller mineralogical picture than either could alone. For example, in lacustrine and deltaic analogue samples, Mössbauer detected nanophase iron oxides that were absent

from the XRD patterns. This difference likely reflects XRD's insensitivity to poorly crystalline and amorphous phases, which may be important in organic preservation.

Raman spectroscopy, while useful for organic identification, showed limitations when detecting iron oxides—particularly when grain size decreased. This is an important consideration for in-situ planetary analyses, where fine-grained materials are common.

In carbonaceous chondrite samples, only Mössbauer spectroscopy was applied, yet its advantages were clear. The technique's ability to provide detailed iron mineralogy without significant sample destruction means that valuable extraterrestrial materials can be analysed without compromising their integrity for subsequent investigations. Based on this, Mössbauer spectroscopy should be prioritised for returned samples to establish a mineralogical baseline. Raman spectroscopy could then be applied with optimised parameters to avoid laser-induced mineral transformations that might destroy organic molecules.

The observation that poorly crystalline iron oxides sometimes coincide with elevated organic content aligns with terrestrial studies demonstrating that minerals such as ferrihydrite possess high sorptive capacities for organic molecules (Lalonde et al., 2012). However, the absence of a universal correlation in analogue samples indicates that mineralogy alone is an insufficient predictor of preservation potential. This supports observations from Mars, where CheMin XRD has identified amorphous iron phases in Gale Crater sediments, yet SAM's detection of organics remains sporadic (Freissinet et al., 2015). This reinforces the need to consider depositional setting, diagenetic alteration, and exposure history alongside mineralogical data.

7.3. Implications for Mars Exploration and Sample Return

For rover-based exploration, the results stress the importance of contextual mineralogical assessment. Reactive iron phases should be regarded as one element within a broader suite of indicators, rather than as a singular predictor of preservation potential. Sites combining reactive iron with fine-grained sediments, low-oxidant geochemistry, and clear evidence of past aqueous activity are more likely to yield preserved organics.

The design of future rover payloads must also take into account the challenges posed by reactive iron species. The presence of these minerals can complicate mineralogical measurements, and without the ability to reliably identify them, interpretations of organic

detections—or absences—remain incomplete. For example, if reactive iron phases catalyse organic degradation during analysis, this could lead to underestimation of organic abundance.

7.4. Limitations and Sources of Uncertainty

This study's conclusions are tempered by several limitations. Mössbauer spectroscopy, while powerful, is restricted to ^{57}Fe -bearing minerals; XRD cannot detect amorphous phases; and Raman spectroscopy is prone to fluorescence interference in iron-rich contexts. Sequential extraction methods can preferentially dissolve certain phases, potentially skewing reactivity profiles.

Natural variability in analogue and meteoritic samples introduces uncertainty, as does the inherent challenge of extrapolating laboratory-scale observations to the geological timescales relevant to Mars. Additionally, in-situ measurements on Mars may face further complications from dust coatings, grain size effects, and instrument sensitivity limits.

7.5. Future Work

Future research should expand the range of analogue environments, incorporating acidic, cryogenic, and hyperarid sites to better capture the diversity of Martian conditions. Advanced high-resolution techniques, such as synchrotron-based Mössbauer spectroscopy and nanoSIMS, could help to directly image organic–iron associations at the microscale.

Long-duration laboratory simulations under Mars-like conditions would provide critical insights into the long-term stability of these associations. Furthermore, systematic studies varying environmental parameters—such as redox state, pH, and temperature—could help disentangle the complex interplay between preservation and degradation processes.

7.6. Conclusion

This research has shown that reactive iron phases can, under the right circumstances, contribute to the preservation of organic matter in Martian-like environments. However, their mere presence is not a definitive indicator of preservation potential. Instead, reactive iron must be interpreted within the broader geological, mineralogical, and geochemical context.

By integrating multiple analytical techniques and applying them in a careful sequence, scientists can maximise the information extracted from both analogue studies and precious extraterrestrial samples. These findings provide actionable guidance for future Mars missions and contribute to refining the scientific approach to the search for life beyond Earth.

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8. Conclusions

This research investigated the role of reactive iron species in the preservation of organic matter under conditions relevant to Mars. By drawing on terrestrial analogue materials, carbonaceous chondrites, and a suite of complementary analytical techniques, it sought to evaluate the advantages and limitations of different mineralogical approaches for identifying reactive iron species and to consider how such identifications could inform our understanding of preservation potential in Martian environments.

The work has demonstrated that reactive iron species are both widespread and highly variable in their impact on organic matter survival. Through the integration of multiple datasets—from Mössbauer spectroscopy, X-ray diffraction (XRD), Raman spectroscopy, and sequential extraction experiments—it has been possible to examine mineral–organic relationships at a level of detail that single-technique approaches could not achieve. These findings are relevant not only to interpreting past and current conditions on Mars, but also to shaping the sampling strategies and analytical priorities of future planetary exploration missions.

1. Reactive iron phases are common but variable in preservation potential

Poorly crystalline iron oxides, such as ferrihydrite, and Fe–sulphides were identified in a range of analogue and meteoritic samples. In a few cases, these minerals occurred in association with measurable organic carbon, consistent with their known ability to adsorb and encapsulate organic compounds. However, the association was not universal: some samples containing abundant reactive iron phases showed little to no detectable organic carbon. This variability suggests that iron mineralogy, while potentially significant, cannot be used as a sole predictor of organic preservation potential. Environmental history, redox conditions, and grain-scale mineral–organic relationships likely all play critical roles in determining whether reactive iron acts as a preservative or a catalyst for degradation.

2. Multiple analytical techniques are essential for accurate interpretation

Each technique used in this study provided distinct and complementary insights into iron mineralogy and its relationship with organic matter. Mössbauer spectroscopy excelled at detecting and quantifying iron-bearing minerals, including nanophase and poorly crystalline phases invisible to XRD. XRD, in turn, offered high confidence in identifying crystalline phases and refining mineralogical context. Raman spectroscopy, while limited by fluorescence interference in iron-rich samples, was valuable for organic detection under the right conditions.

Sequential extraction revealed patterns in iron phase reactivity, occasionally correlating with changes in organic carbon content, and offered a way to experimentally probe mineral–organic interactions.

This combination of techniques highlights the danger of over-reliance on any single method. For future Mars sample analysis, the results suggest that Mössbauer spectroscopy should be employed early in the analytical sequence to establish a baseline mineralogical framework, followed by targeted Raman spectroscopy under carefully controlled parameters to avoid laser-induced alteration of minerals and destruction of organics.

3. Implications for Mars exploration and sample return

The findings have direct implications for both in-situ Mars rover science and the planning of Mars Sample Return campaigns. Reactive iron phases should be considered within a wider preservation framework that also accounts for sedimentary facies, depositional environment, co-occurring mineral phases (e.g., clays, silica), and indicators of low-oxidant conditions. Sites exhibiting these combined characteristics are more likely to retain ancient organics in a detectable form.

Additionally, rover payload designs must address the analytical challenges posed by reactive iron phases. These minerals can complicate spectroscopic measurements and, in some cases, catalyse the destruction of organic molecules during analysis. Without the ability to reliably identify and account for reactive iron, interpretations of organic detections—or absences—remain incomplete. Integrating mineralogical and geochemical context into biosignature searches will be essential for maximising scientific return.

4. Broader scientific significance

Beyond its immediate application to Mars exploration, this research contributes to a broader understanding of the interplay between mineralogy and organic preservation in planetary environments. It refines the criteria by which samples—whether collected on Earth, in meteorite falls, or by planetary missions—can be evaluated for preservation potential. Furthermore, it provides a methodological framework for interpreting upcoming mission results, particularly from *Perseverance*, *Rosalind Franklin*, and Mars Sample Return, in the context of the long-standing search for evidence of past life.

By showing both the promise and the limitations of reactive iron phases as preservation agents, this study adds nuance to our understanding of habitability and biosignature preservation beyond Earth. It underscores the importance of integrated, multi-technique analyses and

situates reactive iron as one component in a much larger geological and geochemical system that governs the survival of organic matter over geological timescales.