The role of sulfate minerals in the search for evidence of life on Mars

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PhD thesis
Mars global image from NASA/JPL-Caltech (2013)
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James Michael Timothy Lewis

Supervisors: Prof. Mark Sephton & Dr. Matthew Genge
Abstract

Spacecraft sent to Mars have revealed that some ancient martian environments were habitable for life. Attempting to detect the organic matter that this potential life may have left behind has been a priority for several missions. However, the search for both biotic and abiotic organic compounds on Mars has yielded only organochlorines, which have an ambiguous origin. Recently it has been recognised that perchlorate (ClO₄⁻) salts found on the surface of Mars are interfering with the heating experiments used by rovers and landers to search for organic matter. The potential for other oxygen-containing salts to disrupt thermal experiments has received comparatively little attention. In this thesis it is shown that the iron sulfate mineral jarosite thermally decomposes and releases oxygen at temperatures that would interfere with the detection of macromolecular organic matter. Experiments using synthetic jarosite samples revealed that during thermal decomposition sulfur dioxide and oxygen are released concurrently at a ratio of 2:1. In the presence of organic matter only the sulfur dioxide is detected, along with the carbon dioxide resulting from the combustion of carbon compounds. Prolonged exposure to water eventually causes jarosite to decompose into goethite. It was found that goethite can retain organic matter that was originally preserved in jarosite. The results demonstrate that though jarosite should be considered a problematic mineral for thermal experiments on Mars, goethite deposits in close proximity to jarosite may be good targets for organic matter detection. Jarosite and goethite have been observed on Mars by both rovers and orbiters. The transition from a habitable world to the present environment was marked by volcanism that created jarosite-forming, acidic, sulfur-rich conditions. The improved knowledge of the thermal extraction of jarosite and goethite containing samples will therefore be relevant in the analysis of a significant part of Mars’ geological history.
Extended abstract

Observations from the orbiters, landers and rovers sent to Mars indicate periods of significant water activity in the planet’s early history and that some ancient martian environments were habitable for life (Ehlmann et al., 2011; Grotzinger et al., 2012; Mahaffy et al., 2012; Williams et al., 2013; Vaniman et al., 2014). However, the search for organic matter that might record the abiotic and potentially biological carbon cycles on Mars has so far only yielded simple chlorinated organic molecules, which have an ambiguous origin (Biemann et al., 1977; Ming et al., 2009; Glavin et al., 2013; Leshin et al., 2013). Within the technological constraints of mission payloads thermal extraction is the most durable and practical method to search for organic compounds on the surface of other planetary bodies (Biemann et al., 1977; Guinn et al., 2008; Mahaffy et al., 2012). Heating can liberate fragments of organic matter from a material of interest but any mineral that releases oxygen at similar temperatures could potentially oxidise organic molecules and render organic matter undetectable (Ming et al., 2009). It is therefore of extreme importance that mineral species that release oxygen and interfere with organic compound detection are identified and their impact understood.

This thesis describes and evaluates the influence of sulfate minerals on the detection of carbon compounds through thermal extraction. Sulfates are salts containing sulfur and oxygen that are abundant on the martian surface (Ehlmann et al., 2009). Perchlorates, another oxygen-containing salt found on Mars, have been the focus of a great deal of recent attention (Chevrier et al., 2009; Hecht et al., 2009; Kounaves et al., 2010b; Kounaves et al., 2014a). Perchlorate salts release chlorine as well as oxygen during thermal decomposition and their influence is one of the hypotheses proposed for the detection of only simple chlorinated organic molecules on Mars (Devlin & Herley, 1986; Ming et al., 2009; Glavin et al.,
Unlike perchlorates the majority of sulfate minerals are relatively stable when heated but iron sulfate species found on Mars, such as jarosite, decompose at temperatures similar to those used to liberate fragments of macromolecular material from samples (Mu & Perlmutter, 1981; Sephton & Gilmour, 2001; Sephton et al., 2004; Frost et al., 2005a; Navarro-González et al., 2006; Sephton, 2012; Sephton et al., 2013). Despite this there has been very little research into the influence of iron sulfates on the detection of trace amounts of organic matter through thermal extraction.

The importance of developing a better understanding of the interactions between sulfates and organic matter during thermal extraction is highlighted by the fact that a significant proportion of Mars’ surface was exposed at a time when sulfate-forming conditions dominated (Bibring et al., 2006; Michalski et al., 2013). The transition from a habitable Mars to the present-day environment was marked by substantial volcanism that released large volumes of sulfur dioxide into the atmosphere (Bibring et al., 2006). The resulting acidic and sulfate rich conditions would have produced iron sulfates and therefore a significant proportion of Mars’ stratigraphy could host minerals such as jarosite (Baron & Palmer, 1996). A better understanding of the influence of jarosite on mission experiments will help the interpretation of existing results, the operation of currently active missions on Mars and the design of future instruments.

Jarosite typically contains a mixture of potassium and/or sodium cations with minor hydronium (Dutrizac & Jambor, 2000; Drouet & Navrotsky, 2003). Natural samples with varying cation abundances were collected through fieldwork. Jarosite-containing materials were sampled from Brownsea Island and St. Oswald’s Bay in Dorset, United Kingdom. The interpretation of natural samples was aided by the synthesis of potassium- and sodium-rich
forms of jarosite in the laboratory. All of the jarosite-containing materials used in this work were characterised by X-ray diffraction (XRD). The thermal decomposition profiles of the different substances were investigated by pyrolysis-gas chromatography-mass spectrometry (py-GC-MS).

The first set of experiments described were designed to establish whether an interaction between decomposing jarosite and organic matter occurs during thermal experiments. The organic carbon content of a natural jarosite clay collected from Brownsea Island was characterised by a combination of solvent extraction, acid-washing and elemental analysis – isotope ratio mass spectrometry (EA-IRMS). It was determined that the sample was carbonate free and contained 0.45% organic carbon, a proportion of which was extractable organic matter. However, during pyrolysis only trace amounts of benzene were detected. Pyrolysis experiments carried out between 400 °C and 1000 °C showed a rise of carbon dioxide with sulfur dioxide with increasing temperature, indicating that decomposing jarosite was oxidising organic matter and preventing its detection. These results clearly demonstrate the negative influence of jarosite decomposition on organic compound detection.

Directly observing and quantifying the release of oxygen during jarosite decomposition required the use of synthetic samples. The fact that both synthetic potassium and synthetic sodium jarosite samples were available also allowed the influence of cation variation on jarosite decomposition to be assessed. The results were compared with the thermal decomposition profiles of natural potassium- and sodium-rich jarosite containing samples collected from St. Oswald’s Bay. A clear correlation between sulfur dioxide and oxygen production was observed in pyrolysis experiments using the synthetic samples, with a cumulative production ratio of 2:1 (sulfur dioxide: oxygen). Oxygen from jarosite
decomposition was not observed in either of the natural samples, with peaks for carbon dioxide seen instead. However, the interpretation of the sodium jarosite containing natural sample was complicated by the presence of crystalline and amorphous carbonate phases. In both natural and synthetic samples potassium jarosite began to decompose at a lower temperature than sodium jarosite. The difference in decomposition temperature was much more pronounced in the synthetic samples, suggesting greater crystallinity and stability in the synthetic samples and fewer impurities. The synthetic jarosite samples were mixed with the organic plastic polyethylene and pyrolysed at 650 °C. When pyrolysed as a single phase polyethylene decomposes to give a series of alkanes, alkenes and dienes. When polyethylene was mixed with jarosite the peaks for compounds containing double bonds decreased dramatically while the response for alkanes was largely unchanged. Jarosite decomposition not only reduces the response for organic matter, it also selectively oxidises compounds. Mixtures of polyethylene and jarosite were also pyrolysed at 500 °C to see if jarosite decomposition could be minimised or avoided at temperatures at which some organic matter should still be liberated. However, when mixed with polyethylene jarosite was seen to decompose more readily and at lower temperatures. Despite this, the response for organic compounds increased slightly at 500 °C when polyethylene was mixed with jarosite compared to pyrolysis of polyethylene as a single phase at 500 °C.

The negative influence of jarosite decomposition on the detection of trace amounts of macromolecular organic material by heating is clearly demonstrated by the work described in this thesis. Like perchlorate, jarosite can be added to the list of problematic minerals for thermal extraction experiments on Mars. The next set of investigations involved experiments to see if the carbon dioxide produced from the interactions between oxidising salts and
organic matter could be diagnostic. Organic matter of low molecular weight is known to break down at a lower temperature than high molecular weight organic matter. When mixed with perchlorate, low weight organic matter (represented by maltenes extracted from an oil) produced a distinct low temperature carbon dioxide peak coupled with oxygen, carbon monoxide, hydrochloric acid and chlorinated organic matter. When medium weight organic matter (represented by asphaltenes from an oil) was mixed with perchlorate a broader profile for carbon dioxide was seen that also correlated with carbon monoxide, hydrochloric acid and organochlorines. High molecular weight organic matter was represented by a solvent-extracted coal. The coal was mixed with perchlorate, jarosite and a mixture of both perchlorate and jarosite. The perchlorate and coal mixture produced a broad high temperature carbon dioxide peak that correlated with carbon monoxide and organochlorines. When the coal was mixed with jarosite the carbon dioxide released produced a sharp high temperature peak and a weak response for simple organic molecules. When jarosite and perchlorate were mixed with the coal oxidation was substantial and the broadest carbon dioxide peak was observed. In addition, chlorobenzene was detected, which was only present in the pyrolysis products when both salts were mixed with the coal. Carbon dioxide peaks were seen to clearly vary with molecular weight. Contamination is typically of a low molecular weight and indigenous organic matter is typically of a high molecular weight. Our observations were applied to data recently collected by Mars Science Laboratory from the Sheepbed mudstone and suggested the mudstone sample contained low weight organic matter.

An acidic sulfate-rich stream discovered in St. Oswald’s Bay allowed the variations in mineralogy and organic chemistry across an active jarosite-forming system to be investigated.
A series of cores were taken across the stream and the layers within each core were separated, allowing the vertical and horizontal variation to be examined. The majority of the study area consisted of a quartz sand with minor clay and jarosite that produced a poor response for organic matter during pyrolysis. In the cores close to the stream a high concentration of jarosite was seen but the oxidising nature of the sulfate meant that the response for organic matter was very poor. On one side of the stream the system was capped with a thin layer of goethite, which gave a much better response for organic matter and yielded compounds including thiophenes. The thiophenes were found to be evidence of natural vulcanisation occurring in the system. The best way to sample iron-sulfate-rich regions on Mars for organic matter may be to target goethite-rich regions in close proximity to jarosite. Goethite is only mildly oxidising during pyrolysis and the chance of a successful detection for organic matter is much greater.

The research described in this thesis has demonstrated that jarosite is problematic for the detection of macromolecular material on Mars. However, unlike perchlorate, it is not globally spread. Avoiding jarosite outcrops entirely would be an unsatisfactory mitigation step as jarosite is associated with liquid water that may have supported martian organisms. Despite the oxidising nature of jarosite demonstrated in this thesis, it was seen that carbon dioxide peaks produced during pyrolysis may permit discrimination of low molecular weight organic matter from high molecular weight organic matter. In addition, experiments on a terrestrial acidic sulfate stream have shown that goethite appears to retain organic matter after forming from jarosite decomposition. Goethite is significantly less oxidising during pyrolysis relative to jarosite. The improved knowledge of the influence of jarosite and goethite on thermal experiments will assist in the interpretation of a substantial part of Mars’ geological history.
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Figure 2.1. The location and geological setting of Brownsea Island. The Parkstone Clay makes up most of the cliffs that run along the southern coast of the island. Map and cross section adapted from Bristow et al., (1991).
Figure 2.2. The thin veneer of jarosite found on the Parkstone Clay to the west of the small bay on the southern coast of Brownsea Island.

Figure 2.3. Much thicker jarosite outcrops were found in a sheltered section of the cliff with overhanging soils and vegetation. At the base of the cliff was a hard iron oxide layer.

Figure 2.4. Hand samples from Brownsea, left: clay with a thin jarosite crust, right: clay with a thick jarosite crust.

Figure 2.5. The location and geological setting of St. Oswald’s Bay and the Lulworth area, geological map and cross section adapted from House (1993).

Figure 2.6. The thin beds of jarosite clay, lignite and iron oxide seen in the Wealden near Durdle Door. The red box denotes the location of the close up image.

Figure 2.7. A decomposed pyrite nodule in the Gault and Greensand in St. Oswald’s Bay. Bright yellow jarosite can be clearly seen in the close up image.

Figure 2.8. Acidic sulfur rich waters flowing out of slumped Wealden beds. These waters precipitate jarosite. An ecological system appears to be present here that is distinct from the surrounding grassy slopes. The stream can be seen flowing parallel to the grassy banks on the left of the photo. On return to this site in 2013 the stream had switched its location to the other side of the jarosite and iron oxide encrusted area.

Figure 2.9. A portion of the jarosite layer found underneath the iron oxide crust.

Figure 2.10. The location and geological setting of the Sandbed Mine in the Caldbeck Fells. The mine is situated within rocks that have been affected by lead, zinc and baryte mineralisation, geological map adapted from Stone et al., (2010).

Figure 2.11. Sandbed Mine viewed looking south onto the Caldbeck Fells. Insets show a closer view of the two mine dumps.

Figure 2.12. Materials collected from the mine dumps at Sandbed Mine. A: A hand specimen at the lower dump site showing a large quartz vein and the fine orange-brown material. B: Material at the upper dump site exhibits a more yellow-orange colour. C: Hand samples collected from the lower mine dump. D: Hand samples collected from the upper mine dump. E: A quartz rich sample with black and turquoise crystals collected from the upper mine dump.

Figure 2.13. The sulfate ecosystem in St. Oswald’s Bay is characterised by a vertically and horizontally highly variable environment. The abundant green matter within the pH 3.5 stream can be clearly seen in this photo and bubbles that were released when the sun was shining on the water can be seen behind the pH strip.

Figure 2.14. Cores taken from across the sulfate stream are labelled 1-9, an additional core was taken from nearby Stair Hole where a similar system appeared to have dried out.

Figure 2.15. This photo shows the main components of the sulfate ecosystem during sampling. In the foreground is clay with a yellow tint due to the presence of jarosite. Beyond the small stream is a hard rusty crust with coverings of moss. There is also a purple microbial mat, which has a distinctive surface sheen.
Figure 2.16. The sampling of core 1. A: The trowel is embedded in the ground at the location where the core was extracted from the grassy clay at the edge of the sample site. B: The extracted core is shown on foil immediately after extraction. C: The frozen core before cutting. D: Vials containing separate portions of the clay and grass.

Figure 2.17. The sampling of core 2. A: The cut made by the trowel can be seen at the transition between the grassy clay and the oxidised surface richer in jarosite towards the base of the photo. B: The extracted core on foil at the sampling site. C: The frozen core, the jarosite enrichment can be clearly seen at the top of the core. D: The vials containing the sandy jarosite clay and the wood fragments with a coating of jarosite.

Figure 2.18. The sampling of core 3. A: The clear layering in this section can be seen in the hole left by core extraction, a clay containing abundant jarosite is capped with a thin iron oxide layer and a slightly thicker purple fibrous microbial mat with a distinctive sheen. B: The extracted core. C: The frozen core, the mat and iron oxide can be seen separated from the homogenous jarosite-rich clay. D: The three vials containing the microbial mat, iron oxide and jarosite clay.

Figure 2.19. The sampling of core 4. A: The trowel is seen stuck in the waterlogged material in the centre of the study area. The hole left from the sampling of core 3 can be seen in the top right. B: The frozen material from core 4 had broken up during transport but the microbial mat, rusty layer and jarosite-rich sandy-clay could still be isolated. C: The isolated layers from core 4 in their respective vials.

Figure 2.20. The sampling of core 5. A: The core was cut where the iron oxide crust was relatively thin near to the small stream filled with green biological matter. B: A strong smell of hydrogen sulfide indicated that core extraction had exposed a reducing environment. C: The reduced green iron layer had vanished during storage over a year. D: The vials from the different components of core 5.

Figure 2.21. The sampling of core 6. A: The core was capped with a tough iron oxide layer and moss. B: The top was tough and stuck together but the underlying clay immediately crumbled after extracting the core. C: The sandy core of the nodule can be seen along with the thin yellow jarosite layer capped with iron oxide and moss. D: The four vials that contain the materials sampled from core 6.

Figure 2.22. The sampling of core 7. A: The core was cut from dry soils immediately to the west of the acidic stream. B: Repeated light and dark layers could be seen in the soils. C: The core was not cohesive and crumbled during storage. D: Wooden fragments, an average of the core mineralogy and a jarosite-rich layer were isolated into vials.

Figure 2.23. The sampling of core 8. A: The core was cut from dry sandy material further from the acidic stream than core 7. This material contained lots of wood fragments, in the top right of the photo the wood upon which yellow crystals were found growing (described in 2.2.4.12). B: When cut in half a woody layer was seen bisecting the core. C: When this layer was sliced horizontally a bright yellow jarosite nodule was found. D: The samples taken from core 8 were the sandy-clay above the wood, the jarosite nodule, the material immediately surrounding the nodule, the wooden layer as a whole and the clay beneath the wood.

Figure 2.24. Sampling of core 9. A: The material in this area was dry, sandy and poorly cohesive. B: When cut in half the core was very homogenous with depth. C: The core material was sampled in one vial.
Figure 2.25. Distinct yellow crystals are observed growing on wood fragments in the sandy-clay. B: The crystals, the wood they were growing on and crystal encrusted wood were sampled.

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Figure 2.27. The pressure vessel setup used to synthesise jarosite. Water and sulfate standards were sealed inside the vessel, which was then placed inside a heating jacket. Temperature and pressure could be monitored throughout the experiment using the large pressure gauge on top of the vessel and the digital readout on the heater controller.

Figure 2.28. Powders mounted in flat holders ready for XRD analysis.

Figure 2.29. The Panalytical X’Pert Pro Alpha-1 XRD system during analysis. The flat holder is located in the stand seen through the lower middle of the right-hand door.

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Figure 2.31. Powdered samples are loaded into quartz pyrolysis tubes and secured with quartz wool at both ends. The tube is then placed in the platinum coil of a pyroprobe, shown on the right.

Figure 2.32. The pyrolysis unit is connected to the 6890 gas chromatograph and a 5973 mass spectrometer. The products of pyrolysis pass along a heated line known as the transfer line. The image on the right shows the inside of the GC oven with a simplified representation of the flow from the transfer line inlet to the mass spectrometer. In reality the GC column is typically coiled and 30 metres in length.

Figure 2.33. The 7890A gas chromatograph, coupled to a 5975C mass spectrometer was used to analyse the liquid extract from the natural jarosite clay sampled at Brownsea Island.

Figure 3.1. Variation in cations present within the alunite structure can have a large influence on decomposition temperature, adapted from Stoffregen et al., (2000).

Figure 3.2. Hand specimens collected from Brownsea Island. Clay with a thin veneer of jarosite can be seen on the left while on the right jarosite-rich clay interlayered with iron oxide can be seen in hand specimens collected from the centre of the southern coastline.

Figure 3.3. The production of light gases during pyrolysis of untreated and acid-washed natural jarosite clay. The m/z 28 peak is labelled as CO? as it could be either carbon monoxide or nitrogen; carbon monoxide is inferred as discussed in the text.

Figure 3.4. The chromatogram produced from gas chromatography-mass spectrometry (GC-MS) analysis of the solvent extract of the natural jarosite clay. ?: Peaks that could not be identified with confidence; A: These peaks are alkane chains but the exact chain length could not be resolved.
Figure 3.5. The powdered natural jarosite clay from Brownsea Island. The earthy orange colour is due to the goethite that makes up a significant proportion of the sample.

Figure 3.6. Total ion current chromatograms of the gaseous products released during individual heating experiments of samples of a natural jarosite clay and a lab standard of ferric sulfate hydrate at 600 °C and 1000 °C. The m/z 28 peak is labelled as CO? as it could be either carbon monoxide or nitrogen; carbon monoxide is inferred as discussed in the text. Very minor peaks for oxygen and carbon dioxide were present in the ferric sulfate hydrate experiment at 600 °C but cannot be seen at the scale of the figure. All chromatograms are presented at the same scale.

Figure 3.7. During pyrolysis of the natural jarosite clay with the mass spectrometer scanning in the range 45-550 amu at 600 °C and 700 °C sulfur dioxide was the only major species detected. A very minor peak for benzene is shown in the 2.5-4 min inset for pyrolysis at 700 °C, it is absent at 600 °C.

Figure 3.8. Total ion current chromatograms of the gaseous products during individual heating experiments of lab standards representing the non-sulfate mineralogy of the natural jarosite clay sample. All chromatograms are presented at the same scale.

Figure 3.9. Total ion current chromatograms of the gaseous products during individual heating experiments of lab standards representing other Mars-relevant minerals at 600 °C and 1000 °C. All chromatograms are presented at the same scale.

Figure 3.10. The production of sulfur dioxide, carbon dioxide, possible carbon monoxide and oxygen during the thermal decomposition of samples of natural jarosite clay and a lab standard of ferric sulfate hydrate in individual heating experiments carried out between 400 °C and 1000 °C at 100 °C increments. *The peak areas were normalised by sulfate mass (100% in ferric sulfate hydrate, 5% of sample mass in the natural jarosite clay – from XRD results). The m/z 28 peak is labelled as CO? as it could be either carbon monoxide or nitrogen, carbon monoxide is inferred as discussed in the text.

Figure 3.11. Gases released during heating of Rocknest samples. Plot A shows the most abundant ions diagnostic of specific gases evolved during pyrolysis, plot B shows minor gases evolved during Rocknest run 4 (Leshin et al., 2013).

Figure 4.1. A clay and iron oxide rich sample from Brownsea Island, which hosts jarosite and organic matter, was found to give a very poor response for organic compounds during pyrolysis-GC-MS (Chapter 3). Jarosite on Mars represents a major complication for experiments searching for trace amounts of organic matter through in-situ heating experiments.

Figure 4.2. Diagram illustrating the formation mechanisms of supergene and hydrothermal jarosite deposits. Two oxidation steps for SO2 are required, firstly an interaction with water that produces H2S and H2SO4 and then oxidation of H2S to create the low pH conditions that maintain jarosite stability. On Earth atmospheric oxygen oxidises H2S to H2SO4 and Fe2+ to Fe3+. On Mars atmospheric CO2 reduction to CO is a possible oxidation mechanism. Oxidation occurs in the vadose zone where rocks are unable to buffer the pH (Papike et al., 2006).
Figure 4.3. A sample return mission would allow Earth based laboratories to unlock the full analytical potential of martian jarosite and provide information about the timing of sulfate formation, as well as fluid temperatures and sources (Mattingly & May, 2011).

Figure 4.4. Total ion current chromatograms of the gaseous products released by heating of equal masses of untreated and acid washed jarosite samples at 1000 °C. The m/z 28 peak in 4.4C is labelled as CO? as discussed in the text. PRT contains potassium jarosite while GS contains sodium jarosite.

Figure 4.5. The synthesis reaction for sodium jarosite (Dutrizac & Jambor, 2000).

Figure 4.6. Infrared spectra for potassium jarosite (KJ) and sodium jarosite (NaJ) adapted from Sasaki et al., (1998), who analysed synthetic samples are shown on the left. The bonds and vibrational modes correlating to peaks at different wavenumbers are labelled, hydronium? Indicates O-H stretching inferred to be linked to hydronium in jarosite (Bishop & Murad, 2005; Sasaki et al., 1998; Spratt et al., 2013). The data from this study are shown on the right.

Figure 4.7. The boundary between red iron oxide formed in the vessel headspace and amber yellow jarosite formed in solution can be clearly seen inside the pressure vessel after jarosite synthesis.

Figure 4.8. A single crystal of sodium jarosite is seen in the centre of this image, just to the left of the crosshairs, it is approximately 40 µm across. The red mark is from a pen, which was used to mark the location of single crystal candidates.

Figure 4.9. Unit-cell parameters a vs. c of the K-Na-H3O jarosite series by Basciano & Peterson (2008). The data for this project are plotted and show the relative abundance of potassium, sodium and hydronium in each jarosite sample.

Figure 4.10. The stepped pyrolysis profile for synthetic potassium jarosite (SK). Triplicate experiments with error bars showing standard deviation. *Water is presented as peak area normalised to starting sample mass as the chromatography column used to quantify carbon dioxide, sulfur dioxide and oxygen was not suitable for quantifying water.

Figure 4.11. The stepped pyrolysis profile for synthetic sodium jarosite (SNa). Triplicate experiments with error bars showing standard deviation. *Water is presented as peak area normalised to starting sample mass as the chromatography column used to quantify carbon dioxide, sulfur dioxide and oxygen was not suitable for quantifying water.

Figure 4.12. The stepped pyrolysis profile for the natural potassium jarosite rich sample (PRT). Triplicate experiments with error bars showing standard deviation. *Water is presented as peak area normalised to starting sample mass as the chromatography column used to quantify carbon dioxide, sulfur dioxide and oxygen was not suitable for quantifying water. The m/z 28 peak is labelled as CO? as it is inferred to be carbon monoxide as discussed in the text.

Figure 4.13. The stepped pyrolysis profile for a natural sodium jarosite rich sample (GS). Triplicate experiments with error bars showing standard deviation. *Water is presented as peak area normalised to starting sample mass as the chromatography column used to quantify carbon dioxide, sulfur dioxide and oxygen was not suitable for quantifying water.
Figure 4.14. Comparison of stepped pyrolysis profiles for the jarosite samples. *Water cannot be quantified with the GC column used to quantify carbon dioxide, sulfur dioxide and oxygen so is presented as peak area normalised to sample mass.

Figure 4.15. Laboratory standards and synthetic magnesite were used to better understand results from the jarosite samples. *Water is presented as peak area normalised to sample mass as discussed earlier in the chapter. **Fig. 4.16a shows laboratory standards mixed in the same proportion of phases identified by XRD. *** Fig. 4.16b shows the same mixture but with 0.1 mg of magnesium carbonate and 0.1 mg of magnesium sulfate added to see if these phases could be the amorphous phases inferred to be present in GS by stepped pyrolysis results.

Figure 4.16. Cumulative production of gases during stepped pyrolysis of jarosite samples and laboratory standards.

Figure 4.17. Chromatograms showing the thermal decomposition products of samples of polyethylene and 10:1 mixtures of sodium jarosite and polyethylene at 500 °C and 650 °C. The chromatograms on the right highlight the behaviour of C₁₁ compounds at the different conditions; a: undecane, b: 1-undecene, c: 1-10-undecadiene.

Figure 4.18. Chromatograms showing the thermal decomposition products of samples of polyethylene and 10:1 mixtures of potassium jarosite and polyethylene at 500 °C and 650 °C. The chromatograms on the right highlight the behaviour of C₁₁ compounds at the different conditions; a: undecane, b: 1-undecene, c: 1-10-undecadiene.

Figure 4.19. The peak areas for benzene, toluene, alkanes, alkenes and dienes detected during pyrolysis of polyethylene and polyethylene and jarosite mixtures during pyrolysis at 500 °C and 650 °C.

Figure 4.20. Sulfur dioxide and carbon dioxide production during pyrolysis of polyethylene (P), potassium jarosite (KJ), sodium jarosite (NaJ) and 10:1 mixtures of jarosite and polyethylene at 500 °C or 650 °C. *The peak areas are normalised to the starting mass of jarosite or polyethylene.

Figure 4.21. Peaks for acetic acid, benzene and toluene produced through pyrolysis of the natural samples GS and PRT. All chromatograms are presented at the same scale.

Figure 4.22. Water, carbon dioxide, oxygen and sulfur dioxide production from the Rocknest samples (Leshin et al., 2013).

Figure 4.23. Major volatiles released from the Confidence Hills sample, estimated profiles are used for carbon dioxide, water and sulfur dioxide as the major isotopes saturated the mass spectrometer detector so minor isotopes were used to estimate signal (Franz et al., 2015).

Figure 5.1. Global concentrations of chlorine on Mars as measured by Mars Odyssey (Keller et al., 2006).

Figure 5.2. Oxygen evolved from perchlorate decomposition during heating experiments carried out by the Phoenix lander (Hecht et al., 2009). The carbon dioxide resulting from any potential organic matter oxidation caused by perchlorate or jarosite decomposition may still permit discrimination between indigenous organic matter and contamination.
Figure 5.3. The oil that supplied the maltenes and asphaltenes for this project was sourced from the sandstone in the cliffs of Osmington Mills, seen here during a postgraduate field trip in 2013.

Figure 5.4. The species detected during stepped pyrolysis of magnesium perchlorate, peak areas are normalised against perchlorate mass (in milligrams).

Figure 5.5. The products of the thermal decomposition of a 1:1 mixture of magnesium perchlorate and maltenes, peak areas are normalised to the mass of perchlorate in milligrams.

Figure 5.6. The products of the thermal decomposition of a 1:1 mixture of magnesium perchlorate and asphaltenes, peak areas are normalised to the mass of perchlorate in milligrams.

Figure 5.7. The products of the thermal decomposition of a 1:1 mixture of magnesium perchlorate and coal, peak areas are normalised to the mass of perchlorate in milligrams.

Figure 5.8. The products of the thermal decomposition of a 1:1 mixture of potassium jarosite and coal, peak areas are normalised to the mass of jarosite in milligrams.

Figure 5.9. The products of the thermal decomposition of a 1:1:1 mixture of magnesium perchlorate, potassium jarosite and coal, peak areas are normalised to the combined mass of salt in milligrams.

Figure 5.10. Carbon dioxide production from 1:1 mixtures of perchlorate and (a) low weight organic matter and (b) medium weight organic matter, (c) shows the production of carbon dioxide from high molecular weight organic matter and perchlorate and jarosite, peak areas are normalised to salt mass.

Figure 6.1. The sulfate ecosystem study area was highly variable and consisted of units such as sandy-clay capped by grass, jarosite-rich dry clays, layers of water saturated clays, jarosite and iron oxides capped with microbial mats or moss and a stream rich in biological materials that effervesced in sunlight. A series of cores were taken across the system and labelled by numbers, which are shown in the figure.

Figure 6.2. The hole produced by the extraction of core 2 shows the layering seen to the right of the acidic stream (from the perspective of Figure 6.1). At the surface is a fibrous microbial mat then a thin layer of iron oxide on top of a jarosite containing sandy-clay, which appears less jarosite rich with depth. Water can be seen rapidly refilling the hole.

Figure 6.3. The decomposition of jarosite into goethite (Stoffregen et al., 2000).

Figure 6.4. Chromatograms showing the pyrolysis products of the grass and sandy-clay found in core 1. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence, ane indicates an alkane and ene indicates an alkene.

Figure 6.5. Core 1 immediately after extraction showing the sandy-clay with a cap of grass.

Figure 6.6. Chromatograms showing the pyrolysis products of the wood and sandy-clay found in core 2. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence, ane indicates an alkane and ene indicates an alkene, S indicates siloxanes – material from the chromatography column.

Figure 6.7. The cut made to extract core 2 is seen close to the edge of the sulfate ecosystem at the boundary between sandy-clay dominated sections and sulfur and iron mineral dominated sections.

Figure 6.8. Chromatograms showing the pyrolysis products of the microbial mat, rusty crust and sandy-clay found in core 3. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified.
with confidence, ane indicates an alkane and ene indicates an alkene, S indicates siloxanes – material from the chromatography column.

**Figure 6.9.** The hole cut to extract core 3. The distinct layering of fibrous microbial mat over a thin rusty layer and then a jarosite containing sandy-clay can be clearly seen. Examples of the fragments of wood that can be observed throughout much of the study area can be seen in the top right and the bottom of the image.

**Figure 6.10.** Chromatograms showing the pyrolysis products of the microbial mat, rusty crust and sandy-clay found in core 4. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence and ene indicates an alkene.

**Figure 6.11.** The trowel is shown in place during extraction of core 4. The hole for core 3 can be seen on the right. Core 3 was cut through a covering of microbial mat while core 4 was dug into a partial covering, a small rusty coloured stream also passed over the sampling area.

**Figure 6.12.** Chromatograms showing the pyrolysis products of the wood, rusty crust and sandy-clay found in core 5. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence, ane indicates an alkane and ene indicates an alkene, S indicates siloxanes – material from the chromatography column.

**Figure 6.13.** Core 5 was cut just to the side of one of the small streams that ran over this part of the study area. Like the main stream the water was full of green particulates and highly acidic.

**Figure 6.14.** Chromatograms showing the pyrolysis products of the nodule exterior and interior and sandy-clay found in core 6. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence and S indicates siloxanes – material from the chromatography column.

**Figure 6.15.** The section cut before extraction of core 6 is seen in the centre of the photo, the largest stream that passes through the study area is immediately to the left.

**Figure 6.16.** Chromatograms showing the pyrolysis products of the microbial mat, rusty crust and sandy-clay found in core 7. All chromatograms are presented at the same scale. S indicates siloxanes – material from the chromatography column.

**Figure 6.17.** After digging out core 7 an indistinct layering could be seen between rust/brown coloured layers and light layers.

**Figure 6.18.** Chromatograms showing the pyrolysis products of the materials found in core 8. All chromatograms are presented at the same scale. S indicates siloxanes – material from the chromatography column.

**Figure 6.19.** The hole dug to extract core 8 is seen towards the bottom of the photo. Unlike core 7, which partially filled with water (though not to the extent of that seen in cores 2-6) after digging the core 8 hole remained dry.

**Figure 6.20.** Chromatograms showing the pyrolysis products of the microbial mat, rusty crust and sandy-clay found in core 9. All chromatograms are presented at the same scale. S indicates siloxanes – material from the chromatography column.

**Figure 6.21.** Core 9 is in the foreground of this photo shot across the study area. The sharp contrast between the environments on each side of the stream that runs between cores 6 and 7 can be seen. In the foreground...
the surface and near subsurface is dry and sandy with jarosite increasingly common at the surface closer to the stream. In the background beyond the stream the surface and subsurface are waterlogged and covered mostly with a rusty crust capped with a microbial mat.

**Figure 6.22.** Chromatograms showing the pyrolysis products of the wood fragments and mineral crusts found near core 8. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence, ene indicates an alkene and S indicates siloxanes – material from the chromatography column.

**Figure 6.23.** The wood fragments found near core 8 that had yellow crystals growing on its surface.

**Figure 6.24.** Chromatograms showing the pyrolysis products of the microbial mat, jarosite and rust layers found at Stair Hole. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence and S indicates siloxanes – material from the chromatography column.

**Figure 6.25.** The microbial mat preserved at Stair Hole appeared desiccated however when the core was removed the base of the hole developed a small layer of water. The small stream to the left of the photo was found to have a pH of 5.

**Figure 6.26.** The unit cell of every jarosite phase found in the study areas at 5% abundance or greater is plotted on the axes of Basciano and Peterson (2008). The unit cell parameters a and c allows the potassium, sodium and hydronium abundances to be estimated. PRT indicates the composition of the jarosite collected in the study area in 2012.

**Figure 6.27.** SEM image of an example of a wood fragment with a mineral crust. The elemental composition of each scan area is shown below the image.

**Figure 6.28.** SEM image of the area studied by scans 2 and 5 in Figure 6.27. The elemental composition of each scan area is shown below the image.

**Figure 6.29.** SEM image of the area studied by scan 3 in Figure 6.27. The elemental composition of each scan area is shown below the image.

**Figure 6.30.** SEM image of the JW powder. The elemental composition of each scan area is shown below the image.

**Figure 6.31.** The mineralogy and organic molecule content of the sulfate ecosystem. Though core dimensions and vertical heights are simplified the horizontal distance between the centre of each core is drawn to scale.

**Figure 6.32.** Peak areas for benzene and toluene for pyrolysis of natural jarosite clay samples at different temperatures. *Peaks are normalised to the sample mass before pyrolysis.

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List of abbreviations

Instrumentation and methods

- X-ray diffraction (XRD)
- International Centre for Diffraction Data (ICDD)
- Powder Diffraction File (PDF)
- Pyrolysis-gas chromatography-mass spectrometry (py-GC-MS)
- Mass to charge ratio (m/z)
- Atomic mass unit (AMU)
- Elemental analysis-isotope ratio mass spectrometry (EA-IRMS)
- Scanning electron microscopy (SEM)
- Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)
- Deionised (DI)

Sampling

- Pequeño Río Tinto (PRT)
- Gault and Greensand (GS)
- Synthetic potassium jarosite (SK)
- Synthetic sodium jarosite (SNa)

Mars and planetary science

- Mars solar day (Sol)
- Polar layered deposits (PLD)
- Recurring slope lineae (RSL)
- Galactic Cosmic Rays (GCRs)
- Solar Energetic Particles (SEPs)

Missions and instruments

- Mars Global Surveyor (MGS)
- Mars Exploration Rovers (MERs)
- Mars Exploration Rover-A (MER-A) (Spirit)
- Mars Exploration Rover-B (MER-B) (Opportunity)
- Mars Reconnaissance Orbiter (MRO)
- Mars Science Laboratory (MSL)
• Exobiology on Mars (ExoMars)

• Infrared Interferometer Spectrometer (IRIS) (Mariner 9)

• Radioisotope Thermal Generator (RTG) (Viking)
• Initial Computer Load (ICL) (Viking)
• Touchdown (TD) (Viking)
• X-ray Fluorescence Spectrometry (XRFS) (Viking)
• Thermal volatilisation-gas chromatography-mass spectrometry (TV-GC-MS) (Viking)

• Imager for Mars Pathfinder (IMP) (Pathfinder)
• Alpha-Proton X-ray Spectrometer (APXS) (Pathfinder) (MERs) (MSL)
• Atmospheric Structure Investigation/Meteorology (ASI/MET) (Pathfinder)

• Mars Orbiter Camera (MOC) (MGS)
• Mars Orbiter Laser Altimeter (MOLA) (MGS)
• Thermal Emission Spectrometer (TES) (MGS)
• Magnetometer and Electron Reflectometer (MAG/ER) (MGS)
• Ultrastable Oscillator for Doppler Measurements (USO/RS) (MGS)

• Thermal Emission Imaging System (THEMIS) (Mars Odyssey)
• Gamma Ray Spectrometer (GRS) (Mars Odyssey)

• Observatoire pour la Mineralogie l’Eau, les Glaces et l’Activite (OMEGA) (Mars Express)
• Planetary Fourier Spectrometer (PFS) (Mars Express)

• Panoramic Camera (Pancam) (MERs)
• Miniature Thermal Emission Spectrometer (Mini-TES) (MERs)
• Mössbauer Spectrometer (MB) (MERs)
• Microscopic Imager (MI) (MERs)
• Rock Abrasion Tool (RAT) (MERs)

• High Resolution Imaging Science Experiment (HiRISE) (MRO)
• Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) (MRO)
• Mars Climate Sounder (MCS) (MRO)
• Mars Color Imager (MARCI) (MRO)
• Context Camera (CTX) (MRO)
• Shallow Subsurface Radar (SHARAD) (MRO)
- Robotic Arm (RA) (Phoenix lander) (MSL)
- Thermal and Evolved Gas Analyzer (TEGA) (Phoenix lander)
- Microscopy, Electrochemistry and Conductivity Analyzer (MECA) (Phoenix lander)
- Wet Chemistry Laboratory (WCL) (Phoenix lander)

- Remote Sensing Mast (RSM) (MSL)
- Laser-Induced Breakdown Spectrometer (LIBS) (MSL)
- Remote Micro-Imager (RMI) (MSL)
- Sample Acquisition Processing and handling (SA/SPah) (MSL)
- Powder Acquisition Drill System (PADS) (MSL)
- Dust Removal Tool (DRT) (MSL)
- Collection and Handling for Interior Martian Rock Analysis (CHIMRA) (MSL)
- Organic Check Material (OCM) (MSL)
- Mars Hand Lens Imager (MAHLI) (MSL)
- Dynamic Albedo of Neutrons (DAN) (MSL)
- Radiation Assessment Detector (RAD) (MSL)
- Rover Environment Monitoring Station (REMS) (MSL)
- Chemistry and Mineralogy (CheMin) (MSL)
- Sample Analysis at Mars (SAM) (MSL)
- Quadrupole Mass Spectrometer (QMS) (MSL)
- Tunable Laser Spectrometer (TLS) (MSL)
- Solid Sample-Evolved Gas Analysis (SS-EGA) (MSL)
- N-tert-butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) (MSL)
- Dimethylformamide (DMF) (MSL)
- Tetramethylammonium hydroxide (TMAH) (MSL)
- 2,6-diphenylphenylene oxide (Tenax) (MSL)
Map 1. The landing sites of successful missions to the martian surface are shown on this topographic map of Mars produced by Mars Global Surveyor. The scales are shown on the smaller version of this map in Figure 1.14 (Vaucouleurs et al., 1973; Greeley & Batson, 1990; Wessel et al., 1998; Smith et al., 1999; Albee et al., 2001; Lemoine et al., 2001; Neumann et al., 2001; Smith et al., 2001; Duxbury et al., 2002; Seidelmann et al., 2002; Neumann et al., 2003; Tanaka et al., 2014).
Map 2. Regions of Mars that are mentioned in this thesis are shown on this topographic map of Mars produced by Mars Global Surveyor. The scales are shown on the smaller version of this map in Figure 1.14 (Vaucouleurs et al., 1973; Greeley & Batson, 1990; Wessel et al., 1998; Smith et al., 1999; Albee et al., 2001; Lemoine et al., 2001; Neumann et al., 2001; Smith et al., 2001; Duxbury et al., 2002; Seidelmann et al., 2002; Neumann et al., 2003; Tanaka et al., 2014).
Map 3. Craters and impact basins that are mentioned in this thesis are shown on this topographic map of Mars produced by Mars Global Surveyor. The scales are shown on the smaller version of this map in Figure 1.14 (Vaucouleurs et al., 1973; Greeley & Batson, 1990; Wessel et al., 1998; Smith et al., 1999; Albee et al., 2001; Lemoine et al., 2001; Neumann et al., 2001; Smith et al., 2001; Duxbury et al., 2002; Seidelmann et al., 2002; Neumann et al., 2003; Tanaka et al., 2016).
Map 4. Structural and water related features that are mentioned in this thesis are shown on this topographic map of Mars produced by Mars Global Surveyor. The scales are shown on the smaller version of this map in Figure 1.14 [Vaucouleurs et al., 1973; Greeley & Batson, 1990; Wessel et al., 1998; Smith et al., 1999; Albee et al., 2001; Lemoine et al., 2001; Neumann et al., 2001; Smith et al., 2001; Duxbury et al., 2002; Seidelmann et al., 2002; Neumann et al., 2003; Tanaka et al., 2014].
Map 5. The chasmata that make up the large canyon system of Valles Marineris are shown on this map of Valles Marineris produced by Mars Global Surveyor (Vauclouleurs et al., 1973; Greeley & Batson, 1990; Wessel et al., 1998; Smith et al., 1999; Albee et al., 2001; Lemoine et al., 2001; Neumann et al., 2001; Smith et al., 2001; Duxbury et al., 2002; Seidelmann et al., 2002; Neumann et al., 2003; Tanaka et al., 2014).
Map 6. Major volcanoes and the volcanic provinces that are mentioned in this thesis are shown on this topographic map of Mars produced by Mars Global Surveyor. The scales are shown on the smaller version of this map in Figure 1.14 [Vaucouleurs et al., 1973; Greeley & Batson, 1990; Wessel et al., 1998; Smith et al., 1999; Albee et al., 2001; Lemoine et al., 2001; Neumann et al., 2001; Smith et al., 2001; Duxbury et al., 2002; Seidelmann et al., 2002; Neumann et al., 2003; Tanaka et al., 2014).
Chapter 1 - A review of the geology and exploration of Mars
Mars global image from NASA/JPL-Caltech (2013)
1.1 Introduction to the thesis

Beginning with the first orbiting probe sent to Mars in 1971 a series of highly successful missions has revealed a dynamic and complex planet, with the data sent back by orbiters, landers and rovers providing new insight into Mars’ past and present but also highlighting the need to adapt future missions to each new challenge this alien world reveals. Arguably the most significant discovery made so far is that the martian surface and subsurface have experienced significant environmental changes, from conditions with a high level of water activity and occasional catastrophic floods, to the cold, dry, oxidised deserts of today (Ehlmann et al., 2011; Williams et al., 2013). Many of these ancient environments were potentially habitable for life and searching for organic compounds on the martian surface has been a priority for several missions looking for the biochemical remnants this potential life may have left behind (Anderson et al., 1972; Ming et al., 2009; Mahaffy et al., 2012). However, only simple chlorinated hydrocarbons have been discovered so far, which have an ambiguous origin and could be contamination from Earth carried on the spacecraft or from abiotic carbon sources (Biemann et al., 1977; Glavin et al., 2013; Leshin et al., 2013).

Abiotic organic compounds are supplied to the martian surface in many different ways; asteroids, comets and interplanetary dust particles that enter the atmosphere are a continuous source throughout the planet’s history (Atreya et al., 2007). In addition, volcanism and serpentinisation took place in the past and may still persist in some form today (Hartmann, 1999; Ehlmann et al., 2010). It is therefore surprising that organic detection missions have so far failed to produce conclusive evidence even for the preservation of abiotic carbon phases (Biemann et al., 1977; Ming et al., 2009; Glavin et al., 2013). It is possible that the organic compounds that would provide evidence for the abiotic and potentially biotic
carbon cycles on Mars are at levels too low to be detected easily, have been destroyed by processes on Mars, or exist in forms that are difficult to analyse with instrumentation sent to the planet so far (Benner et al., 2000; ten Kate et al., 2005). Another possible complication is the influence of minerals present on the surface of Mars on life detection experiments being carried out by missions such as Mars Science Laboratory’s (MSL) rover Curiosity (Figure 1.1) (Groztinger et al., 2012).

Figure 1.1 Curiosity during assembly at the Jet Propulsion Laboratory. The giant rover is currently searching the martian surface for organic compounds using a variety of techniques, principally through thermal extraction by heating samples to high temperatures and analysing the evolved gases (Grotzinger et al., 2012).

Thermal extraction has been the standard method employed to detect organic molecules on Mars as the restricted space and budget of a mission payload makes wet chemistry extremely difficult (Biemann et al., 1977; Guinn et al., 2008; Mahaffy et al., 2012). Thermal extraction is also a technique that works with regular success on Earth (Mu & Perlmutter, 1981; Sephton & Gilmour, 2001; Sephton et al., 2004; Navarro-González et al., 2006; Sephton, 2012; Sephton et al., 2013). The recent discovery of a possibly global presence of the chlorine- and oxygen-containing salt perchlorate on Mars poses significant problems for any thermal extraction
units operating on the planet as perchlorate thermally decomposes to give oxygen, which can oxidise organic matter and render it undetectable (Figure 1.2) (Ming et al., 2009). A key area of research is whether other minerals on Mars may pose a similar threat. Improving knowledge in this field will aid the interpretation of data from historical missions, help mitigate issues uncovered by present-day operations by Mars Science Laboratory and prepare for future missions employing thermal extraction units, such as the planned Exobiology on Mars (ExoMars) rover (Schulte et al., 2012).

1.2 Planned research

In this PhD thesis the influence of sulfate minerals on life detection experiments using thermal extraction on Mars samples is assessed. The following questions were investigated:

1. Do sulfate minerals exert an influence on thermal experiments searching for organic compounds on Mars?
2. How do different varieties of sulfate minerals decompose and what quantities of oxygen are released during thermal decomposition?

3. Can the carbon dioxide resulting from the interaction between oxidative salts and organic compounds during thermal decomposition distinguish between indigenous organic matter and contamination?

4. How would the organic chemistry and geological record of a sulfate-rich ecosystem appear to a Mars rover’s experiments?

Evidence from meteorites and the martian surface indicate that Mars is a sulfur rich planet where late stage sulfur rich magmatic fluids created sulfide rims that readily weathered to secondary sulfur phases, such as calcium, magnesium and iron sulfates (King & McLennan, 2010). Despite their predominance on Mars the interaction of sulfate minerals with low concentrations of organic matter is not well understood and it is the aim of this thesis to improve our appreciation of the potentially problematic nature of martian sulfates. The research described herein uses field work and laboratory techniques to collect and synthesise Mars relevant sulfur-containing samples. Laboratory methods, such as solvent extraction and pyrolysis-gas chromatography-mass spectrometry (py-GC-MS), were used for organic and inorganic analyses during experiments. X-ray diffraction (XRD), scanning electron microscopy (SEM) and infrared spectrometry were used for sample characterisation. The summary of existing research presented in this chapter is arranged as a chronological review of major missions to Mars, with a focus on the instruments and experiments deployed, the past and present environments on Mars and their habitability and the mineralogy of the surface with a focus on sulfur chemistry. The review highlights how discoveries made on Mars have influenced the design, objectives and operation of subsequent spacecraft and how our understanding of the complex geological history of the planet has evolved.
1.3 A review of the geology and exploration of Mars

1.3.1 The early understanding of Mars

Before there was the capability to send missions to Mars only telescopic observations and speculative modelling could be used to try and understand the planet, however theoretical and empirical observations often contradicted one another (Lederberg & Sagan, 1962). Dark surface areas on the red planet were seen to wax and wane, with many scientists believing this was evidence of seasonal vegetation growth, polar caps could also be seen and biologically-favourable temperatures as high as 15 °C were observed (Kuiper, 1957; Sinton, 1957; Sinton & Strong, 1960). However, it was increasingly recognised that if Martians existed they would have to contend with low average temperatures of -62 °C, a lack of large surface water bodies, an absence of abundant molecular oxygen and a thin atmosphere with high ultraviolet radiation flux (Lederberg & Sagan, 1962). The thin atmosphere appeared highly enriched in carbon dioxide relative to the Earth’s atmosphere and dust storms were seen to develop that grew to cover the entire planet (Grandjean & Goody, 1955; Kuiper, 1957). A better understanding of Mars and its potential for life clearly required a close up visit.

1.3.2 Mariner 9: The identification of a dynamic world

The first expeditions to Mars were flyby missions that photographed whatever parts of the planet’s surface were facing the spacecraft as they flew past but their images revealed only heavily-cratered terrain of similar appearance to the lunar crust (McCauley et al., 1972). The apparent lack of dynamic Earth like processes on Mars was enormously disappointing to those who were previously confident that the surface could be an environment amenable to life (McCauley et al., 1972). Despite this disappointment, missions to Mars continued and Mariner 9 became the first probe to orbit Mars on the 14th November 1971 and it immediately
discovered the entire planet was covered in a dusty haze (Masursky et al., 1972). Despite the dust, the orbiter could observe the southern polar cap, a dark spot in an area known as Nix Olympica (later renamed to Olympus Mons) and three dark spots in the Tharsis region (Map 6) that were capped with smooth floored rimless craters, which resembled the calderas seen on terrestrial volcanoes (Masursky et al., 1972). Once the dust storm had ended several large shield volcanoes could be clearly observed (Figure 1.3) as well as multiple lava tubes and channels and steep sided volcanic domes (Greeley, 1973). Some of the shield volcanoes were at least twice as massive as the largest seen on Earth (McCauley et al., 1972), and many of the volcanic surfaces looked fresh and geologically young (Masursky, 1973).

Figure 1.3. A Mariner 9 photo mosaic of Nix Olympica, which would later be renamed to Olympus Mons. The shield volcano is approximately 600 km across and was part of a wealth of evidence that showed that Mars was volcanically active for a substantial part of its history (McCauley et al., 1972).
Aeolian processes were seen to dominate the erosion of present-day Mars, with saltation being the major process but a suspension of fine dust in the atmosphere also led to deposition of sediment in polar regions, large basins and crater floors (McCauley, 1973). Streaks of blown dust indicated that martian winds flow away from the polar regions (Figure 1.4) and are modified by the Coriolis force, with large dust storms originating in the southern latitudes near the Hellas basin before migrating west (Map 3) (Arvidson, 1974). This suspended dust could be detected as broad absorption features by Mariner 9’s Infrared Interferometer Spectrometer (IRIS) (Curran et al., 1973).

Atmospheric water in the form of water ice crystals was detected (Hanel et al., 1972; Curran et al., 1973), but by far the most significant set of observations related to water on Mars were a diverse range of channels unrelated to volcanism (Figure 1.5), with larger channels showing bars and braiding typical of running water, along with smaller channels that could have formed by runoff from precipitation and dendritic canyon systems that were suggestive of ground water sapping (Masursky, 1973; Milton, 1973). Mapping of small channels (between 1 and 10 km) showed they occurred predominantly on heavily cratered plains units in the
southern hemisphere, with the high crater densities indicating ancient terrain, suggesting major episodes of channel formation occurred early in Mars’ geological history (Pieri, 1976).

Structural features such as grabens indicated doming and stretching of the crust and blocky chaotic terrains suggested breaking up and slumping of older geological units (McCauley et al., 1972). A great equatorial chasm (Map 4), which would be later named as Valles Marineris after Mariner 9, had faulted plateaus to the west and large patches of chaotic terrain to the east from which large fluvial channels originated and flowed northwards (Masursky, 1973). A global crustal dichotomy was observed between heavily cratered southern highlands and smooth northern lowlands (Map 2) (Masursky, 1973). The earlier flyby missions had been extremely unlucky and only imaged those areas that were heavily cratered and Moon-like (Figure 1.6), the success of Mariner 9 highlighted the value of an orbiting observatory that

![Figure 1.5. A 400 km channel in Mare Erythraeum imaged by Mariner 9 (Map 2) (Milton, 1973).](image-url)
could image the entire planet and wait out observational problems such as dust storms (McCauley et al., 1972). Though images from Mariner 9 were of variable quality and resolution a global geological map could be assembled with relative ages inferred from the density of cratering on surfaces (Tanaka, 1986). Three stratigraphic systems were defined and named after representative regions with good exposure, the Noachian, after Noachis Terra, consisted of ancient, rugged and heavily cratered terrain, the Hesperian system, named after Hesperia Planum, began at the base of ridged plains material and the youngest, the Amazonian, after Amazonis Planitia (Map 2), was smooth and only moderately cratered (Tanaka, 1986).

The imaging and measurements conducted by Mariner 9 revealed that faulting, volcanism, water and wind have been active forces on Mars for a significant part of its history (Hanel et al., 1972). These are dynamic processes that create a range of diverse habitats and, if they
were present, would have mixed the organic compounds that are the precursors to life (Hanel et al., 1972). Mariner 9's hugely successful mission reignited interest in the potential for life to exist, or have existed, on Mars. The probe's findings ensured that the next mission to Mars would consist of two orbiters paired with landers and that organic compound and life detection would be major mission priorities.

1.3.3 The Viking missions: Looking for life

1.3.3.1 Mission design

The Viking landers aimed to identify organic substances in the top 10 cm of the surface of Mars through heating experiments that would also provide information about mineralogy and hydration via the evolution of gases such as water, carbon dioxide and sulfur dioxide (Figure 1.7) (Anderson et al., 1972). Mimicking terrestrial laboratory experiments on Mars involving wet chemistry was beyond the technological and economic resources of the mission, instead thermal volatilisation with or without thermal degradation was selected as the simplest and most reliable approach to liberate organic compounds from a sample (Biemann et al., 1977). If organic compounds were preserved on Mars it was theorised that they should be expelled by heating of samples at 150 °C, 300 °C and 500 °C with the evolved gases swept into the carrier gas stream of a gas chromatograph interfaced to a mass spectrometer (Anderson et al., 1972). The Viking sample ovens had material delivered to them through a sieve, then the valves sealing the oven were opened thirty seconds before heating and closed immediately afterwards (Biemann et al., 1977). The gas chromatography column was designed to maximise the separation of water and carbon dioxide from organic compounds and was held at 50 °C for 12 minutes followed by a linear increase to 200 °C over 18 minutes and then held at this temperature for up to 54 minutes (Biemann et al., 1977). The interface between the
gas chromatograph and mass spectrometer (GC-MS) included an effluent divider that was designed to prevent the entry of large volumes of gas that would damage the mass spectrometer (Biemman et al., 1977). The instrument was shown to work well on Antarctic soil samples, which were considered a close analogue to martian soils (Biemann et al., 1977).

The Viking biology experiments were designed to test whether martian organisms were limited by the availability of water, would be best detected under martian conditions or whether they may be dormant heterotrophs that would be stimulated by the addition of nutrient mixtures (Sagan & Lederberg, 1976; Klein, 1977). The gas exchange biology

Figure 1.7. Plan view of Viking lander 1 showing the spacecraft, surface materials and sampling operations. RTG: radioisotope thermoelectric generator, ICL: Initial computer load, TD: Touchdown, XRFS: X-ray fluorescence spectrometry (Shorthill et al., 1976).
experiment operated in two modes, the first was known as humid-non-nutrient mode where samples were incubated in the presence of the martian atmosphere and 0.5 ml of nutrient solution (under conditions in which the nutrient does not come into direct contact with the samples) for 7 days (Klein, 1977). The second mode was known as wet-nutrient mode and involved the direct addition of a solution containing organic compounds and inorganic salts (Klein, 1977). The pyrolytic release experiment assumed that martian organisms would have evolved to use carbon dioxide or carbon monoxide and convert them to organic matter due to their presence in the atmosphere; samples were incubated for 5 days in light or dark at a temperature range of 10-18 °C and the gas headspace monitored (Klein, 1977). The labelled released experiment assumed that heterotrophic organisms are present on Mars and would decompose simple organic compounds labelled with radioactive $^{14}$C that would produce radioactive carbon dioxide (Klein, 1977). X-ray fluorescence spectrometers (XRFS) were present on each lander, which permitted an inorganic chemical investigation of martian surface materials (Toulmin et al., 1973).

1.3.3.2 Geological observations

The Viking orbiter 1 spacecraft showed very little water vapour in the atmosphere in the southern hemisphere with a gradual increase across the equator to northern latitudes, the season was northern midsummer and it corresponded to beginning of the water vapour cycle in this hemisphere with a strong diurnal cycling between the solid and vapour phases observed (Farmer et al., 1976). Over a martian year the entire global abundance of water vapour varied between about 1 and 2 km$^3$ of ice (Jakosky & Farmer, 1982). The improved images of the martian surface acquired by the Viking orbiters relative to Mariner 9 allowed
the Noachian, Hesperian and Amazonian to be subdivided into more descriptive epochs (Table 1.1) (Tanaka, 1986).

**Table 1.1 The eight geological epochs of Mars defined by Viking global imaging (Tanaka, 1986).**

<table>
<thead>
<tr>
<th>Epoch</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early Noachian</td>
<td>Major impact-basin formation (Isidis, Hellas, Argyre, and south polar), formation of the northern lowlands (Map 3).</td>
</tr>
<tr>
<td>Middle Noachian</td>
<td>Cratered terrain formation, log normal cratering distribution, faulting in south Tharsis (Map 6).</td>
</tr>
<tr>
<td>Late Noachian</td>
<td>Intercrater plains resurfacing, reduced cratering flux, transition to power-law cratering distribution, intense erosion and runoff-channel development, beginning of intense faulting centred at Syria Planum, formation of highland volcanoes and ridges (Map 2).</td>
</tr>
<tr>
<td>Early Hesperian</td>
<td>Ridged plains emplacement, particularly at Lunae, Syrtis Major, Hesperia, and Malea Planum, and in northern lowlands. Burial and degradation of lowland cratered terrain, extensive faulting centred at Syria Planum, major rifting at Noctis Labyrinthus/Valles Marineris. Alba Mons and Tempe Terra volcanism, fretted channel development, formation of Lowell impact basin (Map 2; Map 3; Map 4; Map 5; Map 6).</td>
</tr>
<tr>
<td>Late Hesperian</td>
<td>Resurfacing of northern plains (by complex of lava flows, aeolian deposits and alluvial sediments), then erosion of these plains. Major volcanism at Tharsis Montes, Alba Mons, Terra Tempe, Syria Planum, Elysium Planitia and Ceraunius Fossae. Outflow channel development by water flooding, deposition of Valles Marineris layered deposits, waning Tharsis tectonism, deposition of south polar unconsolidated material (Map 2; Map 4; Map 6).</td>
</tr>
<tr>
<td>Early Amazonian</td>
<td>Lava flows from northern smooth plains, local volcanic flows at Tharsis Montes, Alba Mons, and Elysium Mons, formation of Olympus Mons aureoles, formation of Lyot impact basin (Map 3; Map 6).</td>
</tr>
<tr>
<td>Middle Amazonian</td>
<td>Continued accumulation of lava flows in northern plains, particularly in Amazonis Planitia, volcanism at Tharsis Montes and Olympus Mons, emplacement of thick, poorly consolidated material at Medusae Fossae formation, development of debris flows and aprons surrounding Deuteronilus and Protonilus Mensae, landslides in Valles Marineris (Map 2; Map 4; Map 6).</td>
</tr>
<tr>
<td>Late Amazonian</td>
<td>Formation of broad flood plains in southern Elysium Planitia, youngest lava flows at Tharsis Montes and Olympus Mons, most recent resurfacing of northern plains, reworking of polar layered, dune, mantle and ice deposits into present form. Debris aprons at Tharsis Montes and Mensae, landslides at Olympus Mons and in Valles Marineris (Map 2; Map 4; Map 6).</td>
</tr>
</tbody>
</table>
The Viking landing sites (Map 1) were selected based on imaging from the orbiters and radar measurements from Earth, the site for Viking lander 1 was a compromise between hazard minimisation and a site of scientific interest while Viking lander 2 was targeted at latitudes where water vapour concentration was a maximum, the optimum location for the biology experiments but more hazardous as the site could not be assessed by radar (Masursky & Crabill, 1976). The Viking mass spectrometers measured the atmosphere during descent and confirmed that carbon dioxide is the main constituent of the atmosphere at all heights below 180 km (Nier & McElroy, 1977), Viking lander 1 landed on a northern equatorial plain named as Chryse Planitia (Map 2) on the 20th July 1976 and Viking lander 2 in an impact basin named as Utopia Planitia on 3rd September 1976 (Map 3) (Nier & McElroy, 1977; Jones et al., 1979). Viking lander 1 returned the first images from the martian surface (Figure 1.8) and revealed a boulder strewn reddish desert on which aeolian and impact processes were immediately evident but there were no indications of macroscopic biology (Mutch et al., 1976b).

Drifts of fine-grained sediment could be seen at the Viking lander 1 site with many occurring in the lee of large boulders (Mutch et al., 1976a). The winds measured at both landing sites were light (a few metres per second) with both solar radiation and convective heat flux from the surface contributing (Hess et al., 1977). Both landing sites were subject to continuous
modification with wind induced entrainment of sediment (Figure 1.9) and condensate formation observed but the overall surface erosion rates appeared to be low (Jones et al., 1979). Erosion also occurred principally in those areas where soil cohesion had been reduced by earlier surface sample activities while the undisturbed surface appeared to be very stable (Arvidson et al., 1983). However, the penetration of the lander feet into the martian surface was indicative of only a weakly-cohesive-fine-grained material (Shorthill et al., 1976).

Both landers observed a substantial amount of red dust in the atmosphere with a mean radius of 1 µm that resulted in a pinkish coloured sky (Mutch et al., 1976a; Mutch et al., 1976b). Variations in atmospheric pressure were linked to condensation and sublimation of carbon dioxide onto and from the southern polar cap (Hess et al., 1977). The more northerly located
Viking lander 2 observed the formation of a thin water-carbon dioxide ice condensate layer, which lasted for more than one-third of Mars’ year (Jones et al., 1979). Surface temperatures ranged from 130 K to 290 K while thermal inertia measurements from orbit indicated there were two major components of the martian surface that had high and low thermal inertia respectively, high-albedo regions were found to have a fine particulate covering (Kieffer et al., 1977). Martian fines were found to be principally silicate particles with some admixture of oxides and possible carbonate minerals that were indurated by a sulfate rich intergranular cement (Toulmin et al., 1977). The chemical results for samples of martian fines analysed by XRFS on each lander were remarkably similar, all had high iron, moderate magnesium, calcium and sulfur, low aluminium and very low alkalis and trace elements, suggestive of the weathering products of mafic igneous rocks (Baird et al., 1976). Modelling suggested Mars fines could be a mixture of 80% iron-rich clay and 10% magnesium sulfate, about 5% carbonate and about 5% iron oxides (Baird et al., 1976). The inferred salts in the martian regolith (making up 8-25% of the soil) could be due to concentration by chemical weathering or incorporation of planetary released volatiles, sulfur, chlorine and bromine were all detected and the inferred assemblage was dominated by the formulas (Mg,Na)SO₄, NaCl and (Mg,Ca)CO₃ (Clark & Van Hart, 1981). In general martian temperatures mitigate against the survival of liquid brines (Clark & Van Hart, 1981). Lander thermal experiments could also study the mineralogy of the heated samples by studying inorganic volatiles produced during heating but only carbon dioxide and water were detected at levels of mineralogical significance (sulfur containing species and oxides of nitrogen were also searched for) (Biemann et al., 1977). Some of the gases were probably adsorbed onto mineral surfaces but the partial decomposition of carbonate minerals and clays, goethite or hydrated sulfates were potential contributors, the absence of sulfur containing species suggests sulfur at the Viking lander sites
occurs as a thermally-stable sulfate with a low vapour pressure below 500 °C (Biemann et al., 1977).

1.3.3.3 Searching for life and organic compounds

Each lander was equipped with three ovens but on both spacecraft only two were functional after landing so in total four samples on Mars were excavated (Figure 1.10) and analysed for organic compounds and inorganic volatiles (Biemann et al., 1977).

It had been assumed that meteoritic input and the photochemical fixation of carbon monoxide into organic compounds would have produced detectable levels of organic compounds.
compounds on Mars but they were found to be completely absent (Klein, 1979). At both landing sites indigenous organic compounds were not detected above 2 ppb despite the fact that atmospheric analyses had indicated that the instrument was performing well (Biemann & Lavoie, 1979). A sharp peak in the very first gas chromatograph was identified as methyl chloride at around 15 ppb, other peak like shapes were attributed to changes in the effluent divider status and the volume of material eluting into the column, the only other identifiable compounds were fluorocarbons of the Freon-E type (Biemann et al., 1977). The Freon-E compounds were definitely of terrestrial origin but some or all of the methyl chloride could have been indigenous to Mars, though the lack of other expected compounds like ethyl chloride suggest it was also contamination from Earth, derived from solvents or absorbed traces of methanol and hydrochloric acid (Biemann et al., 1977). At the Viking lander 1 site exposed regolith had been sampled for organic compounds so at the Viking lander 2 site samples that represented a possible duricrust and another sheltered under a rock were sampled, however other than methylene chloride all compounds were identical to the results obtained from blank runs (Biemann et al., 1977).

The Viking biology experiments generally indicated the absence of biology in the samples tested, results from one experiment were consistent with the presence of biology but when combined with the lack of detection of organic compounds a biological explanation seemed unlikely (Klein, 1977). The gas exchange experiment in both humid-non-nutrient and wet-nutrient modes presented no evidence for metabolic activity by heterotrophs and oxygen was yielded in the experiments suggesting that a strong oxidant was present (Klein, 1977). The pyrolytic release experiment showed a small incorporation of radioactive carbon into organic compounds but these were ruled out to be of biological explanation by later repeats (Klein,
The labelled release experiment met criteria that could be described as a positive result, with nonsterilised samples showing an active initial decomposition, while samples heated at 160 °C showed no decomposition (Klein, 1978). However, there was a remarkably uniform production of gas in the labelled release experiments at both lander sites (Levin & Straat, 1977). The absence of organic matter meant a biological explanation was unlikely and the presence of strongly oxidising chemicals was a possible alternative explanation, it was however clear that the Viking experiments could not sufficiently resolve biological from non-biological results (Klein, 1978).

The results of the gas exchange and labelled release experiments suggested that processes destructive to organic compounds occur on Mars (Klein, 1979). The lack of detection of organic compounds, even those sourced from carbonaceous chondrites, suggest organic matter is destroyed at a rate that prevents accumulation, with oxidation by oxidising agents in the soil or photolysis by ultraviolet radiation being possible causes (Biemann & Lavoie, 1979). Simulations of the Viking experiments showed that oxygen was released when metal peroxides or superoxides were treated with water (as may have happened in the gas exchange experiment) and exposure of labelled nutrients in martian surface analogues to ultraviolet radiation resulted in the release of radioactive carbon dioxide (akin to the labelled release experiment) (Ponnampерума et al., 1977). The Viking biology experiments and the cause of the inconclusive organic detection experiments are still being debated nearly four decades later (Navarro-González et al., 2010; Biemann & Bada, 2011) though further analysis of the martian surface was clearly required it would be another twenty years until the next mission reached the red planet.
1.3.4 Pathfinder: Further evidence of a possible warm and wet early Mars

Pathfinder landed on the 4th July 1997 and deployed the mission’s most striking difference from the Viking missions, a small rover named Sojourner (Figure 1.11) (Golombek et al., 1997a). The mission’s payload included the Imager for Mars Pathfinder (IMP), Alpha-Proton X-ray Spectrometer (APXS) and an Atmospheric Structure Investigation/Meteorology Package (ASI/MET) (Golombek et al., 1997a). The landing site was an inferred depositional fan near the mouth of a catastrophic outflow channel called Ares Vallis (Map 1; Map 4) (Golombek et al., 1997b). Ares Vallis offered the prospect of analysing a variety of rock types transported from the ancient cratered highlands, as well as intermediate aged ridged plains and reworked channel deposits (Golombek et al., 1997b).

Upon landing it was apparent the Pathfinder site appeared to have changed little since it was deposited by catastrophic floods around 1.8-3.5 billion years ago (Golombek & Bridges, 2000). The rocky surface was consistent with Ares Vallis being a depositional plain as imbricated rounded pebbles and cobbles, perched rocks and a possible conglomerate were seen that
suggested fluvial processes with liquid water in equilibrium with the atmosphere, indicating a warmer and wetter past (Golombek et al., 1997a). These rounded surface pebbles may have been rounded by Ares flood waters or liberated by erosion of pre-existing conglomerates, if the latter assumption is correct it would imply that water existed elsewhere and earlier than the Ares flood (Matijevic et al., 1997). Measurements of rock compositions suggested a model in which the surface is made up of about 50% basaltic and 50% andesitic igneous rocks with soils being a mixture of the two with the addition of magnesium sulfate and chloride and iron compounds (Wänke et al., 2001). In general, surface rocks were found to be a dark grey colour with a discontinuous coating of bright red dust of similar composition to soils at the Viking lander sites and distinct from the rocks investigated at the Pathfinder landing site, which suggests that Mars soil is a globally deposited unit (Golombek et al., 1997a). The majority of spectra were consistent with the presence of poorly crystalline ferric oxide while darker soils were coarser grained, compacted or mixed with a large amount of dark ferrous materials (Bell et al., 2000). Airborne dust particles appeared to be magnetised by a maghemite stain or cement, which may have been leached from crustal materials by water (Golombek et al., 1997a).

Two distant hills appeared to be streamlined hills and the landing site is situated on a broad gentle ridge that slopes to the northeast, aligned downstream from the Ares and Tiu Vallis floods (Map 4) (Golombek et al., 1997a). The majority of ventifacts appeared to have formed soon after the flood when a large fresh supply of sand size particles would have been available, at that time the wind was blowing to the northwest but at some point it changed towards the southwest, similar to wind directions today (Golombek & Bridges, 2000). Estimates of erosion rates in the Noachian are similar to low continental denudation rates on
Earth, around $10^2 - 10^4$ nm/year, in the Hesperian and Amazonian the rates became exceedingly slow, $10^{-2} - 10^{-1}$ nm/year, suggesting major climate change at the end of the Noachian and the onset of a stable cold and dry climate (Golombek & Bridges, 2000). However, present day dust entrainment still occurs; the mission imaged dust devil vortices crossing the martian surface that were 14-79 m wide and 46-350 m tall with a dust loading of $7 \times 10^{-5}$ kg/m$^3$ (Metzger et al., 1999). Pathfinder was a success not only scientifically but it also demonstrated that the landing and operation of a rover on Mars was feasible (Figure 1.12).

![Image](image.png)

Figure 1.12. The Sojourner rover imaged by the Pathfinder lander, the camera and APXS on the rover allowed close up studies of rocks and surfaces (Golombek et al., 1997a).
1.3.5 Mars Global Surveyor: A complex sedimentary history

Mars Global Surveyor (MGS) entered Mars orbit on the 11th September 1997 carrying the Mars Orbiter Camera (MOC), Mars Orbiter Laser Altimeter (MOLA), Thermal Emission Spectrometer (TES), Ultrastable Oscillator (for radio science) (USO/RS) and Magnetometer/Electron Reflectometer Package (MAG/ER) (Albee et al., 2001). MGS immediately began to acquire high resolution images of the martian surface that showed dunes, sandsheets and drifts with a range of morphologies, compositions and ages (Malin et al., 1998). Basaltic rocks were seen to dominate the southern highlands while basaltic andesites were the most common lithology in the northern lowlands (Albee et al., 2001). One of the mission’s most important observations was that much of Mars, at depths of up to at least several kilometres, is layered and substantial portions of the planet have experienced burial and exhumation (Figure 1.13) (Malin & Edgett, 2001). Several large areas were found to be devoid of impact craters but the rocks these regions are composed of are ancient indicating that they must have been exhumed very recently (Malin & Edgett, 2001).

![Figure 1.13. Layered deposits seen in the Candor Chasma section of Valles Marineris. The image covers 3.3 x 3.1 km (Malin et al., 1998).](image)
TES observations of low-albedo surface materials indicated a four to one mixture of pyroxene and plagioclase with a dust component of approximately 35% (Christensen et al., 1998). The low-albedo materials appeared relatively free of weathering products, including haematite and clay minerals, suggesting that they are relatively pristine samples of igneous rocks (Christensen et al., 1998). Thermal inertia is governed by particle size, rock abundance, bedrock exposure and degree of induration, Viking had detected two distinct regions on Mars, one with high thermal inertia and one with low thermal inertia (Mellon et al., 2000). High resolution mapping by Mars Global Surveyor identified a further moderate to high thermal inertia unit that appears to be indurated fine grained material that is more abundant at lower elevations and occurs at both Viking lander sites (Mellon et al., 2000). The heavily cratered terrains on Mars were observed to be a patchwork of different aged surfaces, the majority dating back to the first billion year of Mars’ history (Malin & Edgett, 2001). The northern lowlands contained structures interpreted as large buried channels consistent with the northward transport of water and sediment to the lowlands before the end of northern hemisphere resurfacing processes (Zuber et al., 2000). These channels appeared to have drained northwards to the lowlands primarily through the Chryse trough (Map 4) (Albee et al., 2001). Signatures of hydrated minerals (clays, carbonates and sulfates) were noticeably absent from emission spectra despite careful analysis of many millions of spectra (Albee et al., 2001). Small gullies were found to have formed in near-contemporary times and their origin continues to be debated (Malin & Edgett, 2001).

Establishing the ages of martian surfaces through impact crater density and diameter indicated that volcanism on Mars persisted into the last 10-15% of the planet’s history (Hartmann, 1999). Topographic and gravity measurements examined the strength of the
lithosphere beneath the ancient southern highlands where the crust is thickest and observations suggested the northern hemisphere was a locus of high heat flow early in Mars’ history (Zuber et al., 2000). The planetary dichotomy (Figure 1.14) was found to fundamentally be a geophysical feature with mantle processes thinning the lithosphere and resurfacing the northern hemisphere in volcanic rock (Malin & Edgett, 2001). Mars does not have an active magnetic field but strong remnant magnetisation features exist in the ancient crust, which suggests an internal dynamo ceased operation early in geologic time (Albee et al., 2001).

Thin ice clouds and hazes were widespread when Mars Global Surveyor began operations but vanished with the onset of a regional dust storm before reappearing gradually after the storm decayed (Pearl et al., 2001). The most opaque clouds were observed over the summits of major volcanic features (Pearl et al., 2001). It was found that surfaces as young as a few hundred million years should reach crater saturation equilibrium at 60 to 100 m, so it is likely Mars has widespread impact produced regolith at least a few metres deep, this substantial amount of fractured material may contribute to the widespread mobile dust and boulder

Figure 1.14. A global topographic map of Mars produced by the MOLA instrument on Mars Global Surveyor shows the planetary dichotomy between southern highlands and northern lowlands (Zuber et al., 2000).
fields of Mars (Hartmann, 1999). Some impact crater rims showed high thermal inertia relative to the surrounding terrain, while many exhibited no thermal inertia signature suggesting the rims have been mantled with dust after impact (Mellon et al., 2000).

1.3.6 Mars Odyssey: Mapping the elements

After entering orbit Mars Odyssey began to undertake its primary mission objectives in February 2002, which were to map the elemental composition of the surface, provide information on mineralogy and morphology and characterise the radiation risk to future human explorers (Saunders et al., 2004). Included on Mars Odyssey’s payload was the Thermal Emission Imaging System (THEMIS) which produced visible to infrared images of the martian surface and revealed lithologically distinct layers of variable thickness that suggested changes in formation environments through time (Christensen et al. 2003). The mission’s Gamma Ray Spectrometer (GRS) made early observations that revealed a hydrogen rich layer in the upper metre of the subsurface of the southern hemisphere and temporal patches of water frost were seen near the northern polar cap (Christensen et al., 2003; Saunders et al., 2004). GRS later identified two regions near the poles that were enriched in hydrogen and consisted of subsurface enriched layers capped by a hydrogen poor layer that thinned polewards (Figure 1.15) (Boynton et al., 2002). The enriched layer correlated with regions of predicted ice stability and was inferred to contain subsurface ice at an abundance of 35 ±15% of the layer by mass (Boynton et al., 2002).

Permafrost regions were found to make up 15% of the martian surface (Mitrofanov et al., 2003), and the lack of bedrock exposure near the poles suggests enhanced mechanical breakdown associated with these frosts (Edwards et al., 2009). Two further regions with high soil water content were detected on the equator at Arabia and Memnonia (Map 2; Map 4)
where the water content was found to reach 10% by mass, the cause was uncertain but the martian poles may have existed at these locations in the past during a period of high obliquity (Mitrofanov et al., 2003).

Figure 1.15. Low epithermal flux (blue) is indicative of high hydrogen concentrations in the global map of epithermal neutron flux produced by Mars Odyssey (Boynton et al., 2002).

The thin high albedo dust covering on Mars was found to be only tens of centimetres in thickness on average (Newsom et al., 2007b). THEMIS revealed spectrally distinct surface deposits consistent with chloride bearing materials throughout low albedo regions in the southern highlands, though these deposits were small they were found to be widespread in middle to late Noachian terrains and also in some early Hesperian terrains (Osterloo et al., 2008). Chlorides commonly precipitate during the evaporation of surface waters or groundwater or during volcanic outgassing (Osterloo et al., 2008). GRS measured the equatorial and midlatitude distribution of chlorine in the near surface of Mars and found a mean concentration of 0.49 wt%, the surface therefore appears significantly enriched in chlorine relative to martian meteorites and previous estimates for bulk composition (Keller
et al., 2006). Chlorine on Mars is not distributed homogeneously, several regions of high and low concentration are present and chlorine appears to be positively correlated with hydrogen and negatively with silicon and thermal inertia (Keller et al., 2006). Aeolian transport of chlorine enriched dust could account for only some of the variability observed, additional mechanisms such as reactions with volcanic exhalations and aqueous activity may explain the chlorine enrichment seen in regions such as Medusae Fossae (Map 4) (Keller et al., 2006). Chlorine in aqueous environments is extremely sensitive to local conditions so for regional scale aqueous processes sulfates are a better indicator (Keller et al., 2006).

GRS observations of Mars’ surficial materials were used to study seven large areas that make up around 14% of the surface that are possible compositional endmembers, they include three regions mantled with surficial materials, some partially covered and rockier and other regions with greater bedrock exposure (Newsom et al., 2007a). In general Mars has very little exposed bedrock with the crust revealed only in small exposures situated in lower albedo regions that have moderate to high thermal inertia (Edwards et al., 2009). Between the seven possible endmembers there are substantial chemical differences that suggest earlier assumptions that surface materials on Mars were globally homogeneous were not completely correct, though GRS data of the Viking and Pathfinder landing sites indicated that they are of similar compositions (Newsom et al., 2007a). To maintain this heterogeneity the soils must be relatively young and sinks must exist, the exploration rovers (described in Section 1.3.8) observed one such mechanism where dust was seen settling into factures and filling depressions (Newsom et al., 2007b). The compositional differences could be due to variations in protolith composition or the extent of alteration and post soil formation processes (Newsom et al., 2007a). GRS results indicated that Mars appears to have undergone large-
scale surface chemical and mechanical processing and reworking (Edwards et al., 2009). Areas mantled in surficial materials are chemically distinct from each other but chemically homogenous within each region for water, chlorine, potassium, thorium and silicon (but not iron) (Newsom et al., 2007a). Areas with more bedrock exposure have lower concentrations of chlorine, potassium and thorium suggesting enrichment of these elements in surface materials took place, possibly by aqueous processes under low pH conditions (Newsom et al., 2007a). Potassium and thorium are depleted significantly in younger terrains suggesting resurfacing magmas were derived from a more evolved and depleted mantle compared to older terrains formed from a more primitive mantle (Hahn et al., 2007). GRS produced the first statistically useful map of the distribution of sulfur on Mars (Figure 1.16) (McLennan et al., 2010). The martian surface is characterised by elevated sulfur concentrations that average 1.76% (equivalent to a concentration of 4.4% for SO$_3$), a value significantly lower than the 6.2% average for SO$_3$ in soils analysed by surface missions, indicating an uneven global distribution of sulfur (McLennan et al., 2010). Hydrogen distribution correlates with that of sulfur suggesting hydrated sulfates account for a significant proportion of the water content of soils in regions where ice is unstable near the surface (McLennan et al., 2010).

![Figure 1.16. Sulfur concentrations in the upper few tens of centimetres of the martian surface overlain on topography. V-1 and V-2 denote the Viking landing sites, PF is Pathfinder and MER-A and MER-B the Mars Exploration Rovers discussed in Section 1.3.8 (McLennan et al., 2010).](image-url)
Sulfur shows a scattered but statistically significant correlation with chlorine but with chlorine preferentially enriched in the near-surface environment (McLennan et al., 2010). Halite would have been among the last minerals to precipitate from the sulfur and chlorine rich brines that are inferred to have existed on Mars; this upward mobility of chlorine suggests low historical water activity on the martian surface, which would have been a problem for near-surface biological activity (McLennan et al., 2010). The correlation of chlorine and hydrogen indicates chlorine’s involvement in the martian hydrologic cycle and the increase in chlorine abundance seen in younger terrains is possibly due to leaching of older terrains and volcanic activity (Hahn et al., 2007). Iron abundance increased with younger apparent surface age suggesting low pH conditions existed at these times, which would have increased the mobility of iron (Hahn et al., 2007).

No thermal signatures indicative of endogenic heat sources were observed by THEMIS suggesting that near-surface volcanism has not occurred in recent times (Christensen et al., 2003). The spatial resolution of THEMIS combined with a large swath width allowed small scale features to be placed in a regional context and for new volcanic features to be recognised, such as fissure and flank vents and lava shields (Mouginis-Mark & Christensen, 2005). Episodes of flooding and water release were seen in the rough-textured aureole that exists around Olympus Mons and braided channels and streamlined islands occurred at high elevations on the southern rift zone of Ascreaus Mons, with water discharge from snowmelt or the remobilisation of degassed volatiles as possible sources (Map 6) (Mouginis-Mark & Christensen, 2005). Valley networks on Hecates Tholus extend from the caldera rim to the base of the volcano with some valleys partly covered by lavas from Elysium Mons while other valleys placed sediment fans on tops of the same flows indicating long periods of water
release and valley formation in the volcano’s easily erodible ash deposits (Mouginis-Mark & Christensen, 2005). Mars Odyssey’s observations of water led to the 2008 Phoenix Lander mission, which would target the hydrogen enriched layers seen near the North Pole (Map 1).

### 1.3.7 Mars Express: An improved understanding of the mineralogical history of Mars

The payload of Mars Express included the Observatoire pour la Mineralogie l’Eau, les Glaces et l’Activite (OMEGA) instrument, which maps the surface of Mars using visible-near infrared hyperspectral reflectance imagery and began operations in January 2004 (Bibring et al., 2005; Gendrin et al., 2005). On a seasonal scale surface compositional variation was observed to be dominated by the transportation, condensation and sublimation of carbon dioxide and water frosts (Bibring et al., 2005). Martian surface water was found to be trapped in two sinks, some as ice in the polar caps and the remainder as surface hydrated minerals, which appear to have been synthesised during the early evolution of Mars (Bibring et al., 2005). OMEGA has observed iron bearing silicates, hydrated phyllosilicates and sulfates but no carbonates, a finding which challenges the theory that carbon dioxide sustained a long-term greenhouse effect enabling liquid water on early Mars (Bibring et al., 2005). From OMEGA evidence it appears that the era in which surface liquid water was stable did not last long enough to enable large amounts of carbon dioxide to be transformed into carbonates, or that carbonate deposits did previously exist but were destroyed by acid weathering (Bibring et al., 2006). Alternatively a thick carbon dioxide rich atmosphere may have never existed on Mars, in the present day the only reservoirs are the thin atmosphere and a thin permanent carbon dioxide ice cap on the southern pole (Bibring et al., 2006).

Phyllosilicates, found in the oldest terrains, were formed by aqueous alteration early in the planet’s history (an era named as the phyllosian, defined by nonacidic aqueous alteration),
sulfates formed predominantly in a second era (the theiikian, acidic aqueous alteration) and the last, the siderikian, which began 3.5 billion years ago, was when the martian environment became dominated by the formation of anhydrous ferric oxides through a slow superficial weathering without liquid water playing a major role (Figure 1.17) (Bibring et al., 2006). The phyllosian is the era most likely to have hosted life and the low levels of subsequent alteration mean biological molecules, structures or other diagnostic features may have been preserved in the clay rich surface or subsurface (Bibring et al., 2006).

Iron bearing pyroxene was the most widely distributed mineral detected by OMEGA but high calcium and low calcium pyroxene were also identified, the former in recent lava flows and the latter in ancient Noachian crust (Bibring et al., 2006). However, many of the younger surfaces, particularly the northern lowlands, do not exhibit the spectral signatures of iron bearing mafic minerals, instead the constituents have been heavily altered by physical weathering, impacts, peroxide activity, or irradiation (Bibring et al., 2006). High albedo regions on Mars have absorption features indicative of oxidised materials but they lack the signatures for hydrated minerals and are dominated by nanocrystalline red haematite or
maghemite, minerals that are easily transported, cohesive, magnetic and do not require liquid water to form (Bibring et al., 2006).

The majority of phyllosilicates on Mars are iron rich but aluminium rich forms are locally dominant and associated with Noachian aged surfaces exposed by impact, faulting and erosion (Bibring et al., 2006). The spectral features seen are typical of iron rich smectites and aluminium rich phyllosilicates such as montmorillonite (Poulet et al., 2005). Martian brines would likely have been enriched in iron and magnesium (Gendrin et al., 2005). Hesperian-aged lavas are essentially water free indicating that mineralisation of hydrated minerals occurred well before their emplacement (Bibring et al., 2006). Catastrophic floods appear to have not formed phyllosilicates; at locations such as Marwth Vallis phyllosilicates are only seen in the surrounding plateaus and the eroded flanks cut by the flood (Bibring et al., 2006).

Surface clay formation would require a long-lasting wet episode but hydrothermal activity, cooling of the mantle, cratering or a supply of water to impact materials could all form subsurface clays that do not require a warm and thick atmosphere (Bibring et al., 2006). The clays are seen to be a bulk component rather than a surface coating (Poulet et al., 2005).

Sulfates are the second major class of hydrated minerals mapped by OMEGA, their formation would have required the evaporation of water and is therefore a near-surface process, with water possibly supplied by outgassing, rise of the water table, massive outflows or hydrothermal activity (Bibring et al., 2006). The dunes of Olympia Undae (Map 2) in the northern circumpolar regions showed infrared absorption indicative of calcium rich sulfates, such as gypsum, perhaps formed by the interaction of acidic snow with calcium rich minerals during volcanic activity or major outflows of salt rich water followed by evaporation (Langevin et al., 2005). Light toned layered outcrops in Valles Marineris, Margaritifer Sinus and Terra
Meridiani show evidence for kieserite, gypsum and polyhydrated sulfates with magnesium sulfate making up around 5% of the martian soil (Figure 1.18) (Map 2) (Gendrin et al., 2005). Extensive sulfate mineral deposits are inferred to have formed in the late Noachian and early Hesperian, the sulfur source being volcanic degassing from Tharsis and the northern plains, a period of peak volcanism that released large amounts of water and sulfur volatiles that rapidly oxidised to sulfuric acid which then precipitated on the surface (Bibring et al., 2006).

Kieserite hydrates readily when exposed to water and does not transform back during periods of desiccation so its presence on Mars is indicative of an apparent lack of repeating cycles of hydration and desiccation since its formation (Gendrin et al., 2005). Smectites are suggestive of a system that sustained prolonged contact between alkali liquid water and igneous materials while sulfate formation favours acidic conditions and does not require the long-
term presence of liquid water, (Poulet et al., 2005). Sulfate formation and clay formation are
two different processes separated by time that reveal two major climatic episodes on Mars
(Poulet et al., 2005). Mars Express also carries the Planetary Fourier Spectrometer (PFS) which
found a methane mixing ratio of 10 ±5 ppbv during measurements carried out between
January and February 2004, with a variation from 0-30 ppbv (Formisano et al., 2004). The
lifetime of methane should be several hundred years so a non-uniform distribution suggests
localised sources or sinks, with possible methane sources being biogenic, hydrothermal
activity, or impact-related processes (Formisano et al., 2004).

1.3.8 The Mars Exploration Rovers: Revealing ancient sulfate-rich acidic waters

1.3.8.1 Introduction

The Mars Exploration Rover (MER) mission consists of two rovers, Spirit (MER-A), which
touched down in Gusev Crater on the 4th January 2004, and Opportunity (MER-B), which has
been studying the Meridiani plains since 25th January 2004 (Map 1; Map 2; Map 3) (Figure
1.19) (Arvidson et al., 2010; Arvidson et al., 2011). The primary mission objectives were
focused on characterising the current and past martian environments and the role of water
in the formation and alteration of the surface and associated crustal materials (Arvidson et
al., 2011). Each rover was equipped with a panoramic camera (Pancam), thermal emission

Figure 1.19. Approximate true colour image of aeolian ripples on the Meridiani Plains and the tracks of the MER-B rover
Opportunity (Squyres et al., 2006).
spectrometer (Mini-TES), alpha-particle X-ray spectrometer (APXS), Mössbauer spectrometer (MB), microscopic imager (MI), rock abrasion tool (RAT) and navigation and hazard cameras (Arvidson et al., 2011).

1.3.8.2 Spirit

Spirit began its mission on soil-covered, rock-strewn, cratered plains underlain by olivine bearing basalts (Arvidson et al., 2006). Gusev Crater was selected as a landing site as water may once have occupied the crater and partially filled it with sediments (Carter & Poulet, 2012). The composition of soils in Gusev Crater were found to be similar to those at previous landing sites, further supporting the theory that martian dust is a globally-mixed unit (Gellert et al., 2004). Rock surfaces exposed by the RAT resembled primitive basaltic conditions but high abundances of bromine indicated possible alteration of surfaces by aqueous activity (Gellert et al., 2004). Spirit highlighted the value of mobility as its discovery of layered granular deposits at the Columbia Hills locality, which were found to have been modified by aqueous fluids during or after emplacement, was made after travelling several kilometres from its landing site (Arvidson et al., 2006). At Columbia Hills Spirit also discovered outcrops rich in magnesium-iron carbonate (making up 16-34 wt%) (Morris et al., 2010). Evidence for carbonate deposits on Mars had previously been sparse, which was a problem for the theory of an early thick carbon dioxide atmosphere because such an environment should have formed abundant carbonate deposits (Morris et al., 2010). However, the Columbia Hills carbonates were interpreted to be of hydrothermal rather than lacustrine origin (Carter & Poulet, 2012). Observations from Mars Reconnaissance Orbiter for Gusev Crater (discussed in Section 1.3.9) were reprocessed and evidence for hydrated clays and carbonates around Spirit’s traverse were found (Carter & Poulet, 2012). Recently an alternative hypothesis for
the Columbia Hills’ carbonate has been proposed as leaching by brines of nearby tephra deposits that then underwent evaporative precipitation, which could explain the carbonate phases and amorphous silicate observed by Spirit (Ruff et al., 2014).

Spirit’s right wheel drive actuator failed on Sol 779 of the mission (a sol being one Mars solar day), which led to increased wheel slippage and sinkage but it was not until Sol 1871, while navigating around a small depression named as Scamander Crater, that the left wheels uncovered a bright soil (Figure 1.20) and sank deeply (Arvidson et al., 2010). Though the rover was never able to extricate itself from this material, the excavated soils turned out to be of significant scientific interest as they were enriched in ferric-sulfates indicative of acidic waters (Arvidson et al., 2010). Though acidic aqueous conditions would not have been as benign as neutral waters acidic hydrothermal waters are known to support thriving microbial communities on Earth (Arvidson et al., 2010).

![Figure 1.20. False colour mosaic from Sols 2163 to 2177 showing the bright sulfate rich soils exposed by Spirit’s extraction attempts. The labels refer to the names of targets to be analysed by the rover (Arvidson et al., 2010).](image)
1.3.8.3 Opportunity

The soils at Opportunity’s landing site in Meridiani Planum were compositionally similar to Gusev Crater but there were minor differences in iron and minor element concentrations which signified the influence of local components (Rieder et al., 2004). Meridiani Planum was chosen as a landing site because Mars Global Surveyor data indicated a high abundance of haematite in the region (Arvidson et al., 2011). The rocks of Meridiani Planum were found to be cross-stratified sandstones formed by aeolian and aqueous reworking of sand grains composed of a mix of fine grained siliciclastics and sulfates (Squyres et al., 2004). The siliciclastics resulted from the chemical alteration of a basalt while the sulfates were a mix of predominantly magnesium and calcium sulfates and the iron sulfate jarosite (Squyres et al., 2004; Squyres et al., 2006). Jarosite is a hydroxide containing sulfate mineral that represents mineralogical evidence for acidic aqueous processes on Mars (Klingelhofer et al., 2004; Morris et al., 2006). In addition to the sulfate rich layered deposits, haematite spherules known as blueberries were discovered (Figure 1.21) (Zolotov & Shock, 2005; Squyres et al., 2006). The haematite signature detected in Meridiani Planum by MGS was found to be the result of these haematite concretions as they formed a surface lag (Arvidson et al., 2011). Simulations show that under present day martian conditions the Meridiani Planum landing site mineralogy could be explained by a short lived and small amount of liquid water (water to rock ratio of less than one, a pH below three and a lifetime of tens of years) (Berger et al., 2009). Speciation calculations show that the formation of a jarosite-goethite assemblage would have required acidic solutions, possibly formed through near-surface aqueous oxidation of pyrite, while the formation of gypsum would require a partial neutralisation of these waters (Zolotov & Shock, 2005). Regional heating of Meridiani Planum may have released sulfide-rich-hydrothermal waters that gave the area its sulfur rich mineralogy (Zolotov & Shock, 2005).
If the Meridiani Planum gypsum was formed due to neutralisation of regional waters then conversion of jarosite to goethite would have occurred and subsequent goethite dehydration could have produced the coarse-grained haematite observed (Zolotov & Shock, 2005). On Earth jarosite only persists on geological timescales in arid environments as it rapidly decomposes to produce ferric oxyhydroxides in more humid climates (Elwood Madden et al., 2004). The presence of jarosite at Meridiani Planum indicates that alteration did not proceed to completion and that arid conditions must have dominated after jarosite formation (Elwood...
Chapter 1 – A review of the geology and exploration of Mars

Madden et al., 2004). Regional scale aqueous alteration appears to have taken place in Meridiani Planum (Arvidson et al., 2011). However, it is debated as to how such widespread evaporite deposits could have formed in the absence of a topographic basin (Andrews-Hanna et al., 2007). An alternative theory to regional liquid water alteration is that the silicate material present at Meridiani underwent significant acid weathering inside an ice deposit formed during a period of high obliquity (Niles & Michalski, 2009). Thin films of water at the mineral ice boundary may have enabled reactions between silicate materials and sulfate rich aerosols in the atmosphere (Niles & Michalski, 2009). Alternatively a deposit of volcanic ash may have reacted with water bearing vapours and condensed sulfur dioxide from fumaroles, if correct such a process would mean conditions at Meridiani were unfavourable to life (McCollom & Hynek, 2005). The hypothesis of regional water deposition and alteration (i.e. evaporite deposits) has difficulty explaining why highly soluble salts are admixed with less soluble salts such as gypsum (Knauth et al., 2005). A further alternative model is a ground hugging flow of rock fragments, salts, sulfides and ice produced by a meteorite impact (Knauth et al., 2005).

When Opportunity reached Victoria Crater it found impact-related stratigraphy preserved in the crater walls along with meteoritic debris near the crater rim (Squyres et al., 2009). Aqueous alteration had occurred, along with haematite-rich concretions that decreased up section indicating variations in groundwater processes (Squyres et al., 2009). Compositional variations observed at Victoria crater mimicked those seen six km away to the north, indicating that water induced alteration at Meridiani Planum was regional in scope (Squyres et al., 2009). At Endeavour Crater the rim deposits were made up of basaltic breccias, which showed highly localised zinc enrichments suggestive of hydrothermal alteration (Squyres et
Gypsum veins were observed while iron sulfates were absent indicating the fluids that existed at Endeavour Crater were somewhat different in chemistry than those involved in the alteration of other parts of Meridiani Planum (Squyres et al., 2012). The enrichment of gypsum at Endeavour Crater would not have required acidic fluids to form and indicates low temperatures have existed since vein emplacement as gypsum persisted rather than dehydrating to anhydrite (Squyres et al., 2012).

Both rovers observed dust deposits on the rover decks that changed during the course of the mission (Arvidson et al., 2006). Dust devils were also detected (Figure 1.22), further indicating that aeolian transport still persists to some degree on Mars, though the equally spaced clasts and surface deposits observed suggest significant erosion and redistribution happens only rarely in the current environment (Arvidson et al., 2006).

Figure 1.22. A navigational camera on Spirit captured this dust devil crossing the martian surface, it was estimated to be around 70-75 m across and each frame was acquired twenty seconds apart (Arvidson et al., 2006).
1.3.9 Mars Reconnaissance Orbiter: Understanding early Mars

1.3.9.1 Introduction

Mars Reconnaissance Orbiter (MRO) underwent orbital insertion on the 10th March 2006 with a payload including the high resolution imaging science experiment (HiRISE), compact reconnaissance imaging spectrometer for Mars (CRISM), Mars climate sounder (MCS), Mars colour imager (MARCI), context camera (CTX), and the shallow subsurface radar (SHARAD) (Taylor et al., 2006).

1.3.9.2 Clays and the Noachian

MRO observations confirmed that clay minerals are widespread in Noachian terrains indicating a long-duration interaction between water and rocks on Mars over 3.7 billion years ago (Figure 1.23) (Ehlmann et al., 2011). Iron-magnesium phyllosilicates are the most common hydrated phase seen across the Noachian highlands (Wray et al., 2009). The dominance of iron-magnesium phyllosilicates and an association with chlorite indicates formation under anoxic, alkaline, high-pH conditions (Ehlmann et al., 2011). Along with the detection of high-temperature phases such as serpentine and analcime, the pervasive presence of clays in large volumes of Mars’s deepest exposed crustal materials suggests water on Mars was predominantly circulating in the subsurface (Ehlmann et al., 2011). Cold, arid conditions may have dominated the martian surface for over 4 billion years, with only transient surface water episodes (Ehlmann et al., 2011). Serpentine is uncommon on Mars but occurs in some impact craters in the southern highlands (Ehlmann et al., 2011). Serpentine is also observed in olivine-rich stratigraphic units near Isidis basin and melange terrains at the Claritas Rise and Nili Fossae (Map 3; Map 4) (Ehlmann et al., 2010). Compositional variations within the iron-magnesium phyllosilicates, along with the presence
of chlorite, kaolinite, illite and muscovite suggest a rich diversity of waters and environments in the Noachian conducive to habitability (Mustard et al., 2008). Chlorite is almost exclusively seen in impact ejecta or the walls, terraces and crustal uplifts of large impact craters suggesting it was formed by impact generated hydrothermal systems or via diagenesis (Wray et al., 2009).

The Mawrth Vallis outflow channel (Map 4) cuts through ancient Noachian terrains and the exposed sequence includes iron and magnesium smectites in light-toned outcrops overlain by hydrated silica followed by montmorillonite and kaolinite (Bishop et al., 2008; Wray et al., 2008). The stratigraphically higher clays could have formed from leaching of iron and magnesium through continuous aqueous events (Bishop et al., 2008). The transition from smectite to aluminium clays is indicative of hydrothermal activity (Bishop et al., 2008). The

![Figure 1.23](image.png)
Argyre basin (Map 3) is a large impact basin in the southern highlands that excavated early Noachian units and provides evidence for the rock layers underlying the region prior to the Argyre impact (Buczkowski et al., 2010). Two distinct layers are revealed, a lower unit enriched in high calcium pyroxene and an upper unit with laterally extensive occurrences of phyllosilicates such as iron and magnesium smectite and chlorite (Buczkowski et al., 2010). Large craters in the northern plains also reveal phyllosilicate assemblages indistinguishable from those in the southern highlands indicating that liquid water once altered both hemispheres of Mars (Table 1.2) (Carter et al., 2010).

1.3.9.3 Carbonates

An ancient warm and thick carbon dioxide atmosphere is often proposed for Mars (Ehlmann et al., 2008a). However, a carbon dioxide rich atmosphere would have formed carbonate minerals during aqueous alteration and carbonate minerals have proven elusive on Mars (Ehlmann et al., 2008a). MRO revealed a rock layer with spectral characteristics indicative of magnesium carbonate in Nili Fossae (Ehlmann et al., 2008a). The carbonate was associated with phyllosilicates and olivine-bearing rocks of either Noachian or early Hesperian age (Ehlmann et al., 2008a). Thin outcrops of carbonate were seen surrounding the Isidis basin (Murchie et al., 2009b). A modification of the instrumental atmospheric correction parameters allowed CRISM to identify carbonates in Gusev Crater (Carter & Poulet, 2012).

The central peak of Leighton Crater (Map 3) contains materials that have been excavated from around six kilometres depth in the martian crust and spectral data reveal evidence for carbonates (with calcite and/or siderite the species inferred to be present) (Michalski & Niles, 2010). Kaolinite group minerals and hydrated iron-magnesium bearing silicates were also observed (smectite-chlorite or smectite-serpentine are described as good candidates for the
lithology present at this locality) (Michalski & Niles, 2010). The Leighton Crater deposit does not appear to be the result of simple serpentinisation of the crust, or impact-related-hydrothermal alteration, because of the presence of a complex mineralogy that includes aluminium-rich deposits (Michalski & Niles, 2010) Alteration may have occurred at depth with carbonate-bearing siliciclastics buried under lavas being altered by heat and interactions with metamorphic fluids before impact deformation (Michalski & Niles, 2010). Ancient layered carbonates may be extensive in the subsurface and the small component of carbonate in martian dust may be from impacts into carbonate rich regions at depth (Michalski & Niles, 2010).

1.3.9.4 Silica, sulfates and the Hesperian

The aqueous alteration in Mars’ early history should have liberated significant amounts of silica but the orbital detection of such deposits had previously proven elusive (Milliken et al., 2008). MRO’s advanced instrumentation combined with an improved knowledge of how to distinguish phyllosilicates, opaline silica and unaltered hydroxylated glasses through visible-near infrared spectroscopy allowed the silica content of Mars’ surface to be reassessed (Milliken et al., 2008). Hydrated silica features were seen in several southern highland craters and in Valles Marineris, where silica was present in stratified units and occasionally in inverted channel deposits (Milliken et al., 2008).

Aram Chaos (Map 4) is a blocky region contained in a large Noachian crater. The outflow of water from Aram Chaos carved the channel on the eastern side of the crater and then flowed north along Ares Vallis (Lichtenberg et al., 2010). Within the crater, an erosional environment transitioned into a depositional environment and unconformable layering of stratigraphic units took place over the chaos terrain (Figure 1.24) (Lichtenberg et al., 2010).
Two major stratigraphic units are deposited over Aram Chaos (Lichtenberg et al., 2010). The oldest was found to have three distinct stratigraphic horizons, firstly monohydrated sulfates with ferric hydroxysulfate (with spectroscopy suggesting a different hydration state from the ferric sulfates found at Gusev Crater and Meridiani Planum) (Lichtenberg et al. 2010). The next stratigraphic layer consisted of monohydrated sulfates and the third layer nanophase ferric oxides with some monohydrated sulfates (Lichtenberg et al., 2010). The youngest stratigraphic sequence was unconformable, darker, indurated and more resistant to weathering and contained polyhydrated minerals, polyhydrated sulfates and crystalline haematite with goethite and ferrihydrite as likely constituents (Lichtenberg et al., 2010).

In certain locations on Mars spectral bands for opaline silica are associated with hydrated sulfates (Milliken et al., 2008). MRO found that silica deposits adjacent to Melas Chasma (Map 5) in Valles Marineris host hydronium bearing iron deficient jarosite, the first ever detection of jarosite from orbit (Milliken et al., 2008). The Melas Chasma iron sulfate and opaline silica are distinct from the lava flows they overlie (Milliken et al., 2008). The presence of hydronium within the jarosite indicates low temperature acidic aqueous conditions at the time of its formation (Milliken et al., 2008). The opaline silica is stratigraphically lower suggesting

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**Figure 1.24.** The stratigraphy of the sulfate deposits in the Aram Chaos region (Lichtenberg et al., 2010).
evaporation of fluids produced by acidic dissolution of basalt (Milliken et al., 2008). In western Candor Chasma (Map 5) monohydrated sulfates and ferric minerals can be distinguished and high in the section polyhydrated sulfates are concentrated in layers suggesting a change in brine chemistry (Murchie et al., 2009a). The presence of bleached and cemented fractures suggest that fluid flow along fractures led to sulfate formation (Okubo & McEwen, 2007). The lateral extent of opaline silica and iron sulfate strata observed around Valles Marineris (Table 1.2) is evidence of regionally extensive, acidic and low temperature aqueous alteration during the late Hesperian and possibly into the Amazonian (Milliken et al., 2008; Weitz et al., 2010). The formation mechanism is similar to that proposed at Meridiani Planum where trapped aeolian dust and sand was lithified by evaporites due to evaporation of a localised groundwater discharge (Murchie et al., 2009a).

Northern Sinus Meridiani has diverse exposures of mono and polyhydrated sulfates and iron-magnesium smectites indicating multiple wetting events, brine recharge and/or fluctuations in evaporation rate (Wiseman et al., 2010). In the large Miyamoto Crater within Sinus Meridiani exhumed materials are consistent with iron-magnesium smectites unconformably overlain by a sulfate- and haematite-rich plains unit (Map 3) (Wiseman et al., 2008). Noctis Labyrinthus (Map 5) is a late Hesperian to early Amazonian network of intersecting linear troughs located on the eastern edge of Tharsis Plateau that shows a diverse range of hydrated minerals with younger iron-magnesium smectites superposed over sulfates (ferric sulfate and jarosite), hydrated silica and aluminium-rich clays (Weitz et al., 2011). The Noctis Labyrinthus mineral assemblage shows the opposite progression to most of Mars suggesting groundwater diversity at this location and a particularly young habitable environment (Weitz et al., 2011).
<table>
<thead>
<tr>
<th>Short name</th>
<th>Aq. minerals</th>
<th>Morphology</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layered phyllosilicate</td>
<td>Al smectite, kaolinite group, Fe/Mg smectite, hydrated silica, Fe oxides</td>
<td>10s-m thick blanket of Al phyllosilicate and hydrated silica overlying Fe/Mg smectite, commonly polygonally fractured; exposed where protective caprock has been removed.</td>
<td>Mawrth Valles and surrounding regions, Nili Fossae; small exposures elsewhere (Map 4).</td>
</tr>
<tr>
<td>Phyllosilicate in intracrater fans</td>
<td>Fe/Mg smectites from drainage basins</td>
<td>Fan-shaped deposit where channel debouches into crater; phyllosilicate typically in lower, tabular strata.</td>
<td>Holden, Eberswalde, Jezero, Terby craters (Map 3).</td>
</tr>
<tr>
<td>Plains sediments</td>
<td>Chlorides and Fe/Mg smectites</td>
<td>Eroded remnants of phyllosilicate-rich deposits in topographic low, sometimes forming piedmont; may be embayed by chloride.</td>
<td>Scattered throughout highland plains in crater floors and intercrater plains.</td>
</tr>
<tr>
<td>Deep phyllosilicates</td>
<td>Phyllosilicates, dominated by prehnite, chlorite, Fe/Mg smectite</td>
<td>Massive or bouldery to layered outcrops in crater walls and central peaks, massifs, and chasma walls and escarpments.</td>
<td>Crater walls and central peaks in highland plains, walls of Valles Marineris (Map 4).</td>
</tr>
<tr>
<td>Carbonate deposits</td>
<td>Magnesium carbonate, possibly some other hydrated phases</td>
<td>Thin bed overlying or grading into olivine-rich rock; superposed by resistant caprock.</td>
<td>Thin outcrops surrounding Isidis basin (Map 3).</td>
</tr>
<tr>
<td>Intracrater clay-sulfate deposits</td>
<td>Kaolinite, hydrated sulfates including alunite and maybe jarosite</td>
<td>Interbedded phyllosilicate and sulfate layers on crater walls forming “bathtub ring” pattern.</td>
<td>Craters in Terra Sirenum (Map 2).</td>
</tr>
<tr>
<td>Meridiani-type layered deposits</td>
<td>Hydrated sulfates, jarosite, haematite</td>
<td>Undeformed layers superposed on cratered terrain; monohydrated or polyhydrated sulfates in various layers; extensive aeolian erosion; some strata rich in haematite.</td>
<td>Terra Meridiani and Aram Chaos (Map 2; Map 4).</td>
</tr>
<tr>
<td>Valles-type layered deposits</td>
<td>Hydrated sulfates, Fe oxides and sulfates</td>
<td>Thick stack of layers infilling chasmata; mostly horizontal bedding deformed by folding and faulting; monohydrated or polyhydrated sulfates in discrete layers; extensive aeolian erosion; some strata rich in Fe oxide.</td>
<td>Valles Marineris including Candor, Melas, Juventae, Tithonium, and Eos Chasmata (Map 4; Map 5).</td>
</tr>
<tr>
<td>Siliceous layered deposits</td>
<td>Hydrated silica including opal, also jarosite</td>
<td>Thin, light-toned, layered deposits; extensive aeolian stripping, inverted stream channels.</td>
<td>Plains surrounding Valles Marineris (Map 4).</td>
</tr>
<tr>
<td>Gypsum plains</td>
<td>Gypsum, other hydrated minerals</td>
<td>Dark, sandy material in part of polar basal unit reworked into dunes</td>
<td>Dark sediments in north polar erg and north polar deposits.</td>
</tr>
</tbody>
</table>
1.3.9.5 Ancient waters and volcanism

MRO observations indicate that the martian surface appears to have been mostly hyprearid, except during the late Noachian when episodic floods incised the numerous highland valley networks (Ehlmann et al., 2011). Holden Crater (Map 3) hosts impact megabreccias unconformably overlain by light-toned phyllosilicates and a dark blocky unit that was emplaced later during high-magnitude flooding when a lake overtopped the crater rim (Grant et al., 2008). Athabasca Valles (Map 4) is an outflow channel that had been inferred to have been carved by catastrophic water floods (Jaeger et al., 2007). However, MRO observations reveal the valley is entirely draped by a thin layer of solidified lava that erupted from a nearby fissure and inundated the channels (Jaeger et al., 2007). This process may have repeated elsewhere and fluvial or lacustrine landforms may in fact be surfaces dominated by lava (Jaeger et al., 2007). Some of the volcanic vents observed by MRO produced effusive products while others generated mainly pyroclastics, and both turbulent and gentle flood lavas are seen (Keszthelyi et al., 2008). However, many areas of Mars are too mantled to allow metre scale volcanic features to be discerned (Figure 1.25) (Keszthelyi et al., 2008).

Figure 1.25. A layered sequence of lava flows in the wall of Coprates Chasma, Valles Marineris. The layers are partially mantled by dust and debris (Map 5) (Keszthelyi et al., 2008).
The Vastitas Borealis formation in the northern plains (Map 2), previously considered as a possible residue of an ancient Mars ocean, was revealed by MRO imaging to be covered in rocks at uniform densities and lacking the light toned layered deposits seen at sites inferred to be of aqueous origin (McEwen et al., 2007). It is however possible that periglacial processes and impacts could have mixed the uniform boulders from depth into the overlying materials and observations of polygonal patterned ground are supportive of this theory (McEwen et al., 2007).

MRO also tested the hypotheses that the lobate ejecta blankets around some martian impact craters are due to fluidisation by water and that impacts could have produced rainfall that eroded Noachian terrains, (McEwen et al., 2007). Channels, alluvial fan like features, debris flows and ponded and pitted materials have been found in several craters and appear similar to features seen in terrestrial impact craters that hit volatile-rich target areas (McEwen et al., 2007). Sections of the martian crust may be rich in ice, water and hydrated minerals that would form muddy debris flows and lower silicate melting temperature (McEwen et al., 2007). Evidence for impact induced precipitation is inconclusive but first order channels at crater topographic peaks are possible evidence (McEwen et al., 2007). Landscapes being fluvially modified by syndepositional effects during impact cratering could explain some Noachain erosion without the need for a warm and wet atmosphere (McEwen et al., 2007). The frequent detection of iron-magnesium phyllosilicates in the rims, ejecta and central peaks of craters in the southern highlands suggests excavation of altered crust from depth by impacts (Mustard et al., 2008).
1.3.9.6 Habitable environments and organic compounds

The most promising sites for organic matter preservation are potential lake basins containing fans or deltas where sediments were deposited (Ehlmann et al., 2008b). Jezero Crater is inferred to have been an open lake basin in which deltas formed (Map 3) (Ehlmann et al., 2008b). The lowest stratigraphic layer in the crater contains iron-magnesium smectites, which appear to record multiple episodes of aqueous activity (Ehlmann et al., 2008b). Observations from MRO highlight the fact that much of Mars’ early geological record is buried and the best place to send rover and lander missions would be regions where ancient crust has been exposed by erosion or impacts. A five kilometre thick sedimentary sequence in a central mound in the Noachian aged Gale Crater captures the upward transition from clay mineral to sulfate/iron oxide forming environment on Mars (Map 3) (Milliken et al., 2010). The sedimentary sequences do not taper towards the current edge of the mound suggesting sediments may have once filled the crater entirely, while the floor of the crater has spectral signatures consistent with basaltic sandstones (Milliken et al., 2010). Negative and positive relief channels and valley-network-like deposits suggest aqueous processes occurred in Gale Crater (Thomson et al., 2011). The sedimentary sequence is divided into two formations (Milliken et al., 2010). A subhorizontal lower layer that varies in thickness, albedo and texture and hosts iron-smectite clays overlain by mono and polysaturated sulfates (with kieserite the most dominant species) and crystalline ferric oxide (Milliken et al., 2010). The more homogenous upper formation dips more steeply and hosts crystalline ferric oxide (Milliken et al., 2010). Crater counting and superposition indicate the lower formation is 3.6-3.8 billion years in age and straddles the Noachian-Hesperian stratigraphic boundary (Thomson et al., 2011). The strongest sulfate signatures occur in the upper-middle portion of the lower
formation, though aluminium or iron sulfates indicative of highly-acidic conditions have not yet been detected in Gale Crater by MRO observations (Figure 1.26) (Milliken et al., 2010).

1.3.9.7 Present day ice and water

The North Pole of Mars, Planum Boreum (Map 2), is covered by a dome of layered ice deposits, the layers consist of a cross bedded (via aeolian processes) basal unit, polar layered deposits (PLD) and the residual cap with its relatively clean water ice composition (Herkenhoff et al., 2007). Dunes in the region are thought to originate from erosion of the basal unit and both the basal unit and the lower PLD appear to be polygonally fractured (Herkenhoff et al.,
Marker beds can be seen within the upper PLD that may record a repeated climate signal (Herkenhoff et al., 2007).

Fretted valleys at the dichotomy boundary between the northern plains and the southern highlands show evidence for glaciation, with observed features including possible lineated valley fills, moraines and trimlines that indicate ice thicknesses of at least 920 m in late Amazonian glaciation events (Dickson et al., 2008). Lobate features adjacent to massifs and escarpments at the dichotomy boundary were revealed by the shallow radar on MRO to be debris covered glaciers that formed in a previous climate conducive to glaciation at middle latitudes (Holt et al., 2008). Radar measurements from MRO indicated that carbon dioxide ice buried within the South Pole layered deposits has a volume of 12,500 km$^3$, an amount that would increase the mass of the atmosphere by 80% if released at a time of high obliquity (Phillips et al., 2011). Radar imaging of the northern Polar Regions reveals laterally-continuous layers with finely spaced reflectors separated by regions of nearly pure ice (Phillips et al., 2008). Repeated layering could be explained by periodicities in Mars’ orbit and rotation similar to the Milankovitch Cycles on Earth (Mars obliquity variation: 120,000 years; climatic precessions: 51,000 years; eccentricity variation: 95,000-99,000 years) (Phillips et al., 2008).

Dunes on Mars appear similar to those on Earth but are subject to a distinctly Mars-like process, the sublimation of carbon dioxide frosts (Hansen et al., 2011). MRO detected morphological changes in northern polar dunes over a Mars year driven primarily by carbon dioxide sublimation at dune brinks that weakened the material and led to changes in the alcoves, gullies and dune aprons observed (Hansen et al., 2011). Other dynamic features observed were recurring slope lineae (RSL), which are 0.5 to 5 m diameter dark markings that appear on equator facing slopes in the southern hemisphere in the southern summer
The observation of young mid latitude gullies is suggested as possible evidence of snow melting during periods of high obliquity (McEwen et al., 2007). However, the gullies lack both hydrated minerals and evidence of frost or ice (McEwen et al., 2007). No change in the hydration state of minerals has been observed between OMEGA and MRO observations suggesting the hydration state of the surface is constant at present (Roach et al., 2009). The high-resolution studies performed by MRO highlight the environmental transition on Mars from clay-forming to sulfate-forming conditions in its distant past. The diverse mineral assemblages observed indicate that these environments were far from uniform and different environmental settings produce different deposits and challenges and have different potentials for organic compound preservation.

1.3.10 The Phoenix lander: The discovery of perchlorate

1.3.10.1 Introduction

The Phoenix lander arrived in the northern circumpolar plains of Mars on the 25th May, 2008 and operated for 150 sols (Map 1) (Ming et al., 2009). The aim of the mission was to analyse the water that was suggested to be present at this location by Mars Odyssey observations, as well as characterising the chemistry of the surface and subsurface materials, the atmosphere and to assess the biological potential of Mars (Guinn et al., 2008). The Phoenix payload included the Robotic Arm (RA), the Thermal and Evolved Gas Analyzer (TEGA) and the Microscopy, Electrochemistry and Conductivity Analyzer (MECA), which included wet chemistry experiments (Guinn et al., 2008). The wet chemistry laboratory (WCL) within MECA had four single-use cells with ion selective electrodes that could measure ion concentrations, total conductivity and redox potential as well as barium chloride crucibles that could measure sulfate through titration (Hecht et al., 2009). The concentrations measured by WCL would be
the minimum leachable ions present in the soils and would not take into account poorly soluble or insoluble species (Kounaves et al., 2010b). TEGA contained eight small ovens that could heat a sample up to 1000 °C, the evolved gases from melting ice and mineral decomposition were then swept to a mass spectrometer by a carrier gas of high-purity nitrogen (Hoffman et al., 2008).

1.3.10.2 Wet chemistry

The 2.4 m RA could excavate trenches into soil deposits and resistive forces encountered indicated that the soils became stronger with increasing depth due to adsorbed water existing as subsurface ice (Figure 1.27), with the strength rapidly decreasing as ice sublimated (Arvidson et al., 2009). The shallow ice table at the site existed at a depth of 5-18 cm and in late summer snowfall and frost blanketed the surface (Smith et al., 2009).

In the wet chemistry experiments (Figure 1.28) carried out by MECA solutions mixed with Mars soils were found to contain dissolved salts and 0.4 – 0.6% perchlorate (ClO$_4^-$) by mass but a discrepancy with conductivity measurements suggested at least one unmeasured ionic species was present (cations were dominated by Mg$^{2+}$ and Na$^+$, with minor K$^+$ and Ca$^{2+}$, while
the anions other than perchlorate included chloride, bicarbonate and sulfate) (Hecht et al., 2009). Sulfate was present at around 1.3 ±0.5 wt% in the soil and was predominantly magnesium sulfate with some calcium sulfate (Kounaves et al., 2010a). Sulfate was found to be depleted relative to values measured elsewhere suggesting at the Phoenix landing site it exists generally in sparingly soluble forms such as calcium sulfate (Kounaves et al., 2010a). The pH of the solution was measured at 7.7 ±0.5 and the addition of nitrobenzoic acid was buffered by the soil (Hecht et al., 2009). There was a distinct lack of soluble iron (Kounaves et al., 2010a). If the soils at the Phoenix lander site had liquid water present at levels greater than or equal to 0.015 g H₂O/g soil conditions would be in the habitable range for known terrestrial halophilic microbes (Kounaves et al., 2010a).

1.3.10.3 TEGA experiments

During heating of samples in TEGA there was an endothermic transition beginning around 725 °C accompanied by the evolution of carbon dioxide, which was attributed to calcium carbonate present at an abundance of 3-5 wt%, which would also explain the soil’s buffering capacity (Boynton et al., 2009). The amount of calcium carbonate observed in the polar soils is most consistent with formation in the past through the interaction of atmospheric carbon dioxide with liquid water films on particle surfaces (Boynton et al., 2009). TEGA did not detect.

Figure 1.28. From left to right, the Phoenix robotic arm is seen delivering a sample to one of the four WCL cells, the middle image shows the locations from which the samples were taken, the first sample (Rosy Red) was mainly surface material while the second and third were acquired from the ice-soil boundary, on the right is a schematic of the WCL interior (Hecht et al., 2009; Kounaves et al., 2010a).
any organic fragments during heating (Ming et al., 2009). A mass 32 peak detected by TEGA’s mass spectrometer evolved between 325 °C and 625 °C and was attributed to oxygen released by the thermal decomposition of perchlorate salts (Figure 1.29) (Ming et al., 2009).

There was a low-temperature water release starting at 295 °C that gradually rose to 735 °C, which was followed by a high-temperature water release, the low-temperature release could be dehydration of hydrous carbonates or sulfates or phyllosilicates, while the high-temperature release could be dehydroxylation of phyllosilicates or serpentine (Sutter et al., 2009). Sulfur dioxide was not detected by TEGA indicating the sulfates at this site were a thermally-stable form, favouring calcium sulfate rather than magnesium and iron sulfates (Golden et al., 2009). The Phoenix landing site is located between significant sources of sulfur dioxide (the Alba Mons volcano (Map 6)) and water (the polar ice cap), volcanically released sulfur dioxide and hydrogen sulfide could have oxidised to sulfuric acid that would react with carbonates to form calcium and magnesium sulfates (Kounaves et al., 2010a). Sulfur was
found at much higher concentrations in Gusev Crater and Meridiani Planum relative to the Phoenix landing site (Golden et al., 2009).

1.3.10.4 The perchlorate problem

The lack of detection of organic fragments in TEGA may well be due to the fact that perchlorate is a very strong oxidiser when heated and carbon compounds may have been combusted; some of the carbon dioxide detected by TEGA could have resulted from this combustion (Ming et al., 2009). Spectral mapping by Phoenix’s surface stereo imager discovered perchlorate salts were locally concentrated in the subsurface perhaps due to the action of thin films of liquid water that transported perchlorate to the subsurface and concentrated it in patches during times of high obliquity (Cull et al., 2010). Alkaline earth perchlorate salts have a strongly exothermic affinity for water, are deliquescent and have eutectic freezing points in the range of -70 °C which would make low temperature brines on Mars possible (Hecht et al., 2009).

Post-flight experiments on a spare WCL unit found the closest result to what was observed on Mars was achieved if the analogue soil mixture contained 60% calcium perchlorate and 40% magnesium perchlorate (Kounaves et al., 2014a). Calcium perchlorate is highly soluble so its existence indicates the region has been dry or stable with minimal or no liquid water interaction since the perchlorate formed (Kounaves et al., 2014a). Perchlorate rich deposits found in the Atacama Desert are the closest in abundance to the perchlorate measured at the Phoenix landing site (Catling et al., 2010). Gas phase oxidation of chlorine volatiles leading to production of perchloric acid can account for the Atacama perchlorate, so gas phase photochemistry is therefore also a possible source for martian perchlorate (Catling et al., 2010). If perchlorate on Mars has a photochemical origin, with the chlorine sourced from
volcanic gases, then perchlorates are geologically recent as substantial volcanism would have produced a reducing atmosphere (Hecht et al., 2009). Perchlorate formation may also be favoured at high latitudes if ice is required as a reaction surface, or the presence of ozone, which is most abundant in the circumpolar regions (Hecht et al., 2009). The formation of calcium-magnesium perchlorate is consistent with atmospherically deposited perchloric acid reacting with calcium and magnesium carbonates, such a process may explain the low levels of exposed carbonates seen on Mars (Kounaves et al., 2014a). The hydrogen levels detected in polar soils by Mars Odyssey may be hydrated forms of perchlorate (Hecht et al., 2009). If other regions of Mars host the majority of chlorine in the form of perchlorate salts then low-temperature brines may be possible elsewhere on Mars (Hecht et al., 2009). A portion of the martian meteorite EETA 79001 hosted perchlorate at 0.6 ± 0.1 ppm, chlorate at 1.4 ± 0.1 ppm, and nitrate at 16 ± 0.2 ppm (Kounaves et al., 2014b).

Results from the Viking lander biology experiments indicated the presence of reactive oxidants, which were believed to be peroxide and superoxide (Quinn et al., 2013). Perchlorate itself is unreactive under the biology experiment conditions but when irradiated it can decompose in carbon dioxide environments to form hypochlorite, trapped oxygen and chlorine dioxide that could explain the Viking observations (Quinn et al., 2013). The fact that chlorate was detected in a martian meteorite supports the hypothesis of radiolysis of Mars perchlorate, with highly oxidised oxychlorines being produced from ultraviolet and gamma radiation (Kounaves et al., 2014b). If such a process is occurring only highly refractory or well protected organic compounds may survive on Mars (Kounaves et al., 2014b). It has been suggested that the chlorinated hydrocarbons detected by Viking may have been the result of perchlorate decomposition (Navarro-González et al., 2010). An analogue experiment using
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Atacama desert soils containing 32 ±6 ppm of organic carbon were mixed with 1 wt% magnesium perchlorate and when combusted formed water and carbon dioxide and small amounts of chloromethane and dichloromethane (Navarro-González et al., 2010). However, such claims were strongly contested by the Viking scientists, particularly due to the lack of chlorinated aromatic molecules in the Atacama data (Biemann & Bada, 2011). Though chlorine values were 0.73% at Chryse Planitia (Map 2) and 0.44% at Utopia Planitia the perchlorate/chloride ratio is unlikely to be identical to the Phoenix Lander site (Map 1) (Biemann & Bada, 2011). The discovery of perchlorate on Mars has a huge influence on the ability of thermal extraction units to detect organic compounds and also on the aqueous environment of present day Mars as liquid brines may well be possible.

1.3.11 Mars Science Laboratory: Analysing ancient habitable environments

1.3.11.1 Introduction and rover design

The Mars Science Laboratory (MSL) mission is centred on the delivery and operation of a rover named Curiosity, which has a payload capacity of 75 kg (Grotzinger et al., 2012). Gale Crater was selected as a landing site as the lower stratigraphy of its central mountain, informally named as Mount Sharp, shows a progression from clay-bearing to sulfate-bearing strata that records the progression through multiple potentially habitable environments (Map 1; Map 3) (Grotzinger et al., 2012). MRO studies revealed several sites of interest within Gale Crater prior to landing which included an alluvial fan within the landing ellipse, a layered rock body with a high thermal inertia and high-albedo, fresh craters that penetrate this high-albedo unit, and strata near the base of Mount Sharp that host hydrated sulfate minerals (Grotzinger et al., 2012).
Curiosity’s payload (Figure 1.30) includes the remote sensing mast (RSM), which provides a view from around two metres above the martian surface and has azimuth and elevation control (Grotzinger et al., 2012). Included in the RSM are the ChemCam, Mastcams and Navcams (Grotzinger et al., 2012). ChemCam consists of a laser-induced breakdown spectrometer (LIBS) coupled to a telescopic camera, the remote micro-imager (RMI) (Grotzinger et al., 2012). LIBS measures the elemental compositions of targets up to seven metres from the rover, and RMI provides the geological context (Grotzinger et al., 2012).

Mastcam is a high definition camera that can characterise and determined the geological history of Gale crater and monitor ice, frost, atmospheric and meteorological events (Grotzinger et al., 2012). The sample acquisition, processing and handling (SA/SPah) subsystem consists of a robotic arm (RA) with turret mounted devices including a powder acquisition drill system (PADS), dust removal tool (DRT), sieves, and a soil scoop that are part of the Collection and Handling for Interior Martian Rock Analysis (CHIMRA) (Grotzinger et al., 2012). A sealed synthetic organic check material (OCM) is on board for experimental controls along with a sample observation tray (Grotzinger et al., 2012). The turret science instruments include an alpha particle X-ray spectrometer (APXS) and Mars Hand Lens Imager (MAHLI) (Grotzinger et al., 2012). The MSL APXS is an improved version of that used on the MERs and Pathfinder, which combines X-ray emission with X-ray fluorescence to characterise rocks, soils, rinds and near-surface layers or veins (Grotzinger et al., 2012). MAHLI examines rocks at hand lens scale as well as imaging drill holes, monitoring frost, searching for fluorescent materials using UV LEDS, and taking rover self-portraits to monitor the rover’s condition (Grotzinger et al., 2012).
The Dynamic Albedo of Neutrons (DAN), Radiation Assessment Detector (RAD) and Rover Environmental Monitoring Station (REMS) measure the depth and abundance of hydrogen and hydroxyl groups in the upper metre of the martian subsurface, the surface radiation and the meteorological conditions around the rover respectively (Grotzinger et al., 2012). CheMin (chemistry and mineralogy) is a powder X-ray diffraction instrument that detects individual mineral phases in complex mixtures present at an abundance of 3% and above, it is the first XRD instrument to operate on another planet (Grotzinger et al., 2012; Vaniman et al., 2014). The Sample Analysis at Mars instrument suite (SAM) makes up 40 kg of the MSL payload and is conducting a sensitive search for organic compounds using thermal or chemical extraction.
on samples collected and sieved by CHIMRA (Mahaffy et al., 2012). SAM consists of three instruments, a quadrupole mass spectrometer (QMS), a gas chromatograph (GC) and a tunable laser spectrometer (TLS) (Grotzinger et al., 2012). The core SAM experiment is solid sample-evolved gas analysis (SS-EGA), to which 59 of the 74 quartz sample cups are dedicated (Mahaffy et al., 2012). Samples are heated to around 950-1100 °C under a helium gas flow with the QMS continuously scanning, gas flow can also be diverted onto a hydrocarbon trap for later GC-MS or TLS analysis (Mahaffy et al., 2012). In addition, SAM can perform combustion experiments for isotope studies or wet chemistry by reacting samples with N-tert-butylidimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) and dimethylformamide (DMF) at 75-300 °C, which derivatizes compounds such as amino acids into species sufficiently volatile for GC-MS analysis, or thermochemolysis below 340 °C using tetramethylammonium hydroxide (TMAH) and methanol for detection of bound polar molecules (Mahaffy et al., 2012; Freissinet et al., 2015a). Terrestrial testing of the wet chemistry procedures found that MTBSTFA reacted rapidly with hydrated minerals and that iron oxides could deactivate derivatized compounds (Stalport et al., 2012). TMAH is more resistant to water reactions so a careful consideration of sample mineralogy will be required before deciding which wet chemistry method to employ on Mars samples (Stalport et al., 2012).

1.3.11.2 Landing and soil analysis at Rocknest

After the rover had successfully landed on the 6th August 2012, APXS measurements revealed a lithologically diverse region named as the Bradbury assemblage, which indicated the mixing of aluminium- and iron-rich components and high-iron contents on the surface of some samples reflected secondary precipitation of iron oxides as a cement or rind (Schmidt et al., 2014). The first sample to be analysed by CheMin and SAM was a soil sample of windblown
dust named as Rocknest (Bish et al., 2013). Initial APXS measurements of Rocknest showed that the soil chemistry in Gale Crater was similar to the MER and Pathfinder soils but with slight enrichments in titanium and iron (Figure 1.31) (Yen et al., 2013). The rocks in Gale Crater were found to have an enrichment in potassium that was not reflected in the soil indicating there is not a strong contribution from local rocks to soil composition in Gale Crater (Yen et al., 2013). CheMin analysis of Rocknest revealed plagioclase, forsteritic olivine, augite and pigeonite, with minor potassium feldspar, magnetite, quartz, anhydrite, haematite and ilmenite as well as a significant amount of X-ray amorphous material that was similar to amorphous phases found on Mauna Kea, Hawaii (Bish et al., 2013).

Figure 1.31. The chemical compositions of Gale Crater, Meridiani Planum and Gusev Crater soils are nearly identical in APXS measurements (Yen et al., 2013).
SAM analysed four separate portions of the Rocknest soil scoop (Figure 1.32; Figure 1.33) (Leshin et al., 2013). Water, carbon dioxide and oxygen evolved during heating and were relatively consistent between the samples but sulfur dioxide varied from run to run suggesting variation in the abundance of sulfur-bearng minerals in each portion, though evolution generally occurred in two main peaks from 500 °C to 550 °C and 700 °C to 750 °C (Leshin et al., 2013).

Oxygen was one of the most abundant gases detected during heating and the onset of its release was simultaneous with that of chlorinated hydrocarbons suggesting oxychlorine salts were decomposing and interacting with organic compounds (Glavin et al., 2013). The fact that...
perchlorates are present at both Gale Crater and at the Phoenix landing site suggests a global formation mechanism and a global spread, with hydrated calcium, magnesium or iron perchlorate inferred to be present at Gale Crater (Archer et al., 2013; Glavin et al., 2013). Oxygen evolution overlaps with the initial rise in sulfur dioxide suggesting oxidation of sulfides while iron sulfates, along with possible sulfites could explain much of the rest of the sulfur dioxide (Leshin et al., 2013).

This was the first detection of evolved sulfur species from a martian surface sample during in-situ EGA (McAdam et al., 2014). Brine activity in the low-humidity conditions on Mars may have provided suitable conditions for the formation of amorphous iron sulfate, which may make up some of the amorphous material measured by CheMin (Sklute et al., 2015). The detected water abundance and release temperature suggested water originated from the amorphous component within Rocknest while decomposition of fine-grained iron or
magnesium carbonates could explain much of the evolved carbon dioxide along with reactions between perchlorate sourced hydrochloric acid and carbonates (Leshin et al., 2013).

During heating of Rocknest and in blanks there was an instrumental background from products of MTBSTFA decomposition indicating that despite the wet chemistry cups being sealed some solvent was leaking out and contacting samples (Franz et al., 2015). MTBSTFA vapour could explain around 10% of the carbon dioxide detected if the derivatization agent was being oxidised during heating (Leshin et al., 2013). SAM GC-MS analysis detected chloromethane, dichloromethane, trichloromethane, chlorobenzene and chloromethylpropene (Glavin et al., 2013; Leshin et al., 2013). The chloromethanes were at abundances significantly higher than Viking measurements and given that these compounds were absent in blanks it is strongly suggestive that chlorination of organic compounds was occurring in the Rocknest sample (Glavin et al., 2013; Leshin et al., 2013).

1.3.11.3 Yellowknife Bay

Pebble- and cobble-sized clasts that were observed at the landing site and along the traverse to the next major study site at Yellowknife Bay were indicative of two end-member transport systems; angular clasts delivered by impacts and rounded pebbles that appear to have been modified by intermittent alluvial or fluvial processes including smaller rounded clasts that are often associated with conglomerate outcrops (Yingst et al., 2013). Climate conditions at the time the sediment was transported must have been substantially different to present-day Mars to permit the sustained aqueous flows that would have enabled mobilisation and modification of these pebbles (Williams et al., 2013). During the traverse ChemCam identified two principal soil types, a hydrated fine grained mafic type representative of widespread martian soils and a locally derived coarser felsic type (Meslin et al., 2013).
Yellowknife Bay is an embayment located five hundred metres to the east of the landing site and it was at this location that the first sample acquisitions by drilling took place in a mudstone layer named as the Sheepbed member (Figure 1.34) (Grotzinger et al., 2015). Two powdered samples were drilled a few metres apart and revealed by CheMin and SAM to contain up to around 20 wt% clay minerals as well as exhibiting magnetite enrichment and olivine depletion; a mineral assemblage best explained by aqueous alteration at circumneutral pH levels combined with a moderate supply of oxidants that existed for hundreds to tens of thousands of years (Vaniman et al., 2014; Bristow et al., 2015; Grotzinger

Figure 1.34. Diagenetic features seen in the Sheepbed member. A: Millimetre scale nodules, interpreted as concretions, are locally abundant in the mudstone, which is also crosscut by sulfate filled fractures. B: Hollow nodules are sometimes voids with raised rims (as indicated by white arrows) or filled with sulfate when intersected by veins (black arrows). C: Raised ridges are the result of infilling cements in rock fractures. D: Sulfate filled fractures are present in the Sheepbed target are consistent with brittle deformation of lithified mudstone followed by precipitation of sulfate from mineralising fluids (Grotzinger et al., 2014).
et al., 2015). The drilled samples, named as John Klein and Cumberland, contained smectite, plagioclase, augite, pigeonite, iron-forsterite, orthopyroxene and magnetite, minor sanidine, bassanite, anhydrite, akaganeite and pyrrhotite along with quartz, haematite, ilmenite, pyrite and halite near detection limits, about a third of each sample was X-ray amorphous (Vaniman et al., 2014). John Klein was intersected with calcium sulfate rich veins while Cumberland was drilled in a section rich in nodules and poor in veins (Ming et al., 2014).

Like Rocknest the most abundant gas evolved during EGA of John Klein and Cumberland was water, the other evolved gases, in order of abundance, were hydrogen, carbon dioxide, sulfur dioxide and oxygen for John Klein and hydrogen, oxygen, carbon dioxide and sulfur dioxide for Cumberland (Figure 1.35) (Ming et al., 2014). Water and hydrogen should be released from adsorbed, interlayer and structural water as well as through dehydroxylation of minerals (Ming et al., 2014). The evolution of both sulfur dioxide and hydrogen sulfide suggests reduced and oxidised sulfur species were present in the samples though the abundance of sulfur bearing gases was significantly lower in both samples relative to Rocknest (Ming et al., 2014).

Figure 1.35. Evolved gas analyses from the John Klein-4 and Cumberland-2 samples. Plots A show the most abundant evolved gases while plots B show evolved trace gases. Some traces have been scaled (Ming et al., 2014).
Iron sulfates are unlikely in the environment preserved at Yellowknife Bay, the observed pyrrhotite and pyrite are potential sources of hydrogen sulfide (Ming et al., 2014). A low temperature oxygen release seen in both samples was attributed to perchlorate or chlorate salts with differences between the two samples suggesting some degree of cation variation (Ming et al., 2014). The simultaneous release of carbon dioxide and oxygen, like that seen in Rocknest, was suggestive of the combustion of organic matter (Ming et al., 2014). EGA detected chloromethane and dichloromethane while SAM-GC-MS analysis detected trichloromethane and carbon tetrachloride (Ming et al., 2014). The Cumberland sample was found to contain significant amounts of chlorobenzene and C₂ to C₄ dichloroalkanes that were above blank levels while Rocknest and John Klein showed levels similar to background (Grotzinger et al., 2015). The presence of oxychlorine compounds were suggested as the cause of the detection of chlorohydrocarbons during EGA (Figure 1.36) (Freissinet et al., 2015b; Grotzinger et al., 2015). Oxidised nitrogen was detected during heating of the samples and was interpreted to represent 110-300 ppm of nitrate in Rocknest, 70-260 ppm in John Klein and 330-1,100 in Cumberland, a biochemically accessible form of nitrogen that could have formed through fixation by thermal shock or volcanic plume lightning (Stern et al., 2015).

Figure 1.36. Chlorobenzene abundance in samples measured by SAM's GC-MS (Grotzinger et al., 2015).
The wet chemistry cups within SAM have yet to be deliberately utilised but the fact that MTBSTFA vapour has been detected in CHIMRA was manipulated to do a preliminary derivatization experiment and a Cumberland sample was sat for 400 sols in the rover so it could react with the vapour (Freissinet et al., 2015a). The sample was heated to 250 °C in an attempt to decompose oxychlorine salts before the main experiment, and then given another 48 hours to react with the MTBSTFA vapour before being heated to 900 °C and the released volatiles sent to the hydrocarbon trap for GC-MS analysis (Freissinet et al., 2015a). High molecular weight compounds significantly above blank levels were detected but the full results have not yet been released (Freissinet et al., 2015a). The chlorinated hydrocarbons seen in EGA and GC-MS analysis of Cumberland cannot be explained fully by instrumental contamination, instead they are interpreted as being the products of reactions between martian chlorine and organic carbon, derived either from martian or exogenous sources, this suggests that reduced carbon materials can survive on Mars despite the abundance of oxidants and exposure to radiation (Freissinet et al., 2015b).

The Cumberland site appears to be an environment that favoured the preservation of organic compounds and nitrate (Grotzinger et al., 2015; Stern et al., 2015). The Yellowknife Bay mudstones in general give evidence of variable redox states, moderate pH and low salinity conditions existing at the time of their formation, which could have supported a microbial community (Vaniman et al., 2014). The fact that the oldest sediments within Gale Crater are now thought to be from the early Hesperian indicates habitable-clay-forming periods may have persisted for longer than previously thought (Grotzinger et al., 2014; Vaniman et al., 2014).
A continuous veneer of dust across the Yellowknife Bay formation outcrops is thought to have prevented the detection from orbit of the significant amount of hydrated clay minerals present in the crater (Grotzinger et al., 2015). The formation is inferred to represent a prograding alluvial fan, fluvio-lacustrine, depositional system influenced by at least two distinct diagenetic events that led to clay formation and later calcium sulfate precipitation in fractures (McLennan et al., 2014). The conversion of olivine into secondary smectite clays seen at Yellowknife Bay, occurring through diagenesis of water-saturated sediment, is a form of clay formation that was not previously recognised on Mars and is in contrast to the weathering and hydrothermal alteration previously considered typical of the planet (Grotzinger et al., 2015). A distal fluvial to lacustrine environment is a prime site for the concentration of organic matter but results so far have not confirmed if the organic matter affected by chlorination reactions is martian in origin (Ming et al., 2014).

1.3.11.4 Jarosite at Confidence Hills

In September 2014 Curiosity drilled three targets (Confidence Hills, Mojave 2 and Telegraph Peak) at a location at the base of Mount Sharp named as the Pahrump Hills, which is a 12 m thick sedimentary section in the Murray formation, the basal geological unit of Mount Sharp (Grotzinger et al., 2015; Rampe et al., 2015). Rocks with an alkaline composition were observed intermittently between the landing site and the Pahrump Hills and appear to originate from a previously unknown martian magma type that is highly alkaline and fractionated (Grotzinger et al., 2015). The Murray formation itself is composed of a complex assemblage of fluvial, deltaic, lacustrine and aeolian deposits (Grotzinger et al., 2015). All of the surface rocks preserved in Gale Crater appear to be sedimentary but of a basaltic constitution and compositionally indistinguishable from igneous rocks previously observed in
situ on Mars (Grotzinger et al., 2015). All three drilled samples contained variable amounts of plagioclase, pyroxene, iron oxides, jarosite, phyllosilicates and X-ray amorphous material (Rampe et al., 2015). The presence of jarosite suggests acid-sulfate alteration that is in stark contrast to the circumneutral pH shallow lake environment preserved at Yellowknife Bay (Rampe et al., 2015). In the Confidence Hills sample CheMin identified haematite, magnetite, a phyllosilicate, multiple feldspars, mafic silicates and minor contributions from sulfur-bearing species, including jarosite (Cavanagh et al., 2015).

EGA analysis of Confidence Hills revealed water, oxygen, carbon and silicon bearing phases at levels undetectable to CheMin (Figure 1.37) (Franz et al., 2015). The carbon dioxide release profile was consistent with contributions from multiple sources and contributions from

Figure 1.37. Major volatiles released from the Confidence Hills sample, estimated profiles are used for carbon dioxide, water and sulfur dioxide as the major isotopes saturated the mass spectrometer detector so minor isotopes were used to estimate signal (Franz et al., 2015).
MTBSTFA were minimised by heating the sample at an isothermal temperature to boil off any contamination prior to analysis (Franz et al., 2015). Jarosite can explain a sulfur dioxide evolution seen around 580 °C while an aluminium sulfate in the amorphous phase may explain the remainder (McAdam et al., 2015). Unlike any other sample previously heated Confidence Hills evolved oxygen near 775 °C, a release possibly related to sulfate or perchlorate decomposition (McAdam et al., 2015). A unique high temperature carbon dioxide release occurred at 725 °C and 775 °C that was suggested as possible evidence of combustion of organic matter but further data are required to be certain (McAdam et al., 2015).

1.3.11.5 The martian atmosphere and radiation

<table>
<thead>
<tr>
<th>Gas</th>
<th>Volume mixing ratio (QMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0.960 (±0.007)</td>
</tr>
<tr>
<td>Ar</td>
<td>0.0193 (±0.0003)</td>
</tr>
<tr>
<td>N₂</td>
<td>0.0189 (±0.0003)</td>
</tr>
<tr>
<td>O₂</td>
<td>1.45 (±0.09) x 10⁻³</td>
</tr>
<tr>
<td>CO</td>
<td>&lt;1.0 x 10⁻³</td>
</tr>
</tbody>
</table>

Isotopic measurements using the TLS within SAM provided further evidence that Mars lost a great deal of its atmosphere early on, with atmospheric reservoirs being established around 4 billion years ago (Mahaffy et al., 2013; Webster et al., 2013). Initially Curiosity could only set an upper limit for martian methane but after 20 months of observations data analyses revealed a background methane level of 0.69 ±0.25 ppbv and a 60 sol period of elevated methane levels at 7.2 ±2.1 ppbv (Webster et al., 2015). These observations imply at least two sources of methane on Mars, the stable background from the continuous decomposition of meteoritic organic compounds by radiation (Webster et al., 2015). The source of the elevated
methane is highly debated and could be due to a release from subsurface ice, water-rock reactions or perhaps life (Webster et al., 2015). Residual organic compounds on the exterior of the rover would not be a significant source of methane when exposed to UV radiation however experiments found that the large amount of kapton tape on the rover could be a significant source of methane contamination but only early in the mission (Schuerger et al., 2011).

RAD monitored the galactic cosmic rays (GCRs) and solar energetic particles (SEPs) interacting with the martian surface, GCRs can penetrate up to several metres depth while SEPs are sporadic but generally do not reach the surface (Hassler et al., 2014). Radiation may play a key part in the chemical alteration of the martian regolith and exposed rocks over geological timescales as well as affecting organic molecule preservation (Hassler et al., 2014). It is therefore the case that recently exposed rocks or soils would be the best prospects for organic compound detection (Hassler et al., 2014). RAD measurements found that accessing any viable radioresistant microbial cells that may have gone through reanimation within the last 450,000 years would require drilling to one m depth rather than the two m previously predicted (Hassler et al., 2014). In addition the survival of organic matter in carbonaceous chondrites that land on Earth demonstrates that meteoritic material can survive ionising radiation for billions of years (Hassler et al., 2014).
1.4 A brief history of Mars exploration

**1971 Mariner 9 orbiter**

- Channels inferred to have been shaped by fluvial processes were found to be common in ancient heavily cratered highlands.
- A range of volcanic landforms, faults and chaotic terrains were observed.
- Present day Mars is modified predominantly by aeolian erosion.
- Discovered a crustal dichotomy between southern highlands and smooth northern lowlands.
- Global imaging defined a stratigraphic system consisting of the Noachian, Hesperian and Amazonian.

**1976 Viking orbiters and landers**

- Higher resolution orbiter images relative to Mariner 9 subdivided the Noachian, Hesperian and Amazonian into more detailed epochs and thermal inertia measurements identified two major surface components with high and low thermal inertia.
- Ruled out the presence of macroscopic organisms on the surface. The results of lander biology experiments looking for microbes were largely negative and where results were apparently positive it was instead attributed to oxidants present in the martian soil rather than life.
- The lander was able to measure the atmosphere and detect organic contaminants present in the spacecraft but the only organic compound detected that was possibly from the martian surface was methyl chloride.
- Winds on the surface were light and even during dust storms the mobilisation of dust on the surface was minimal during the observation period.
- Water and carbon dioxide ice frosts were seen and variations in atmospheric pressure were attributed to carbon dioxide condensing and sublimating from the southern polar cap.
- Martian fines were found to have high iron, moderate magnesium, calcium and sulfur and low aluminium, and very low alkalis and trace elements.

**1997 Pathfinder lander and rover**

- Pathfinder landed on a depositional plain formed by an ancient catastrophic flood and discovered imbricated pebbles and possible conglomerates and streamlined hills.
- Soil composition was similar to the Viking soils suggesting Mars soil is a globally deposited unit.
- Post-Noachian erosion rates appear to be very low.
- Demonstrated that rovers can operate successfully on the surface of Mars.

**1997 Mars Global Surveyor orbiter**

- Discovered that much of Mars, at depths of up to at least several kilometres, is layered and has experienced burial and exhumation. Some regions appear to have been exhumed very recently.
- Discovered a third thermal inertia unit with a moderate to high thermal inertia interpreted to be indurated fine material.
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- Large channels near the equator indicated the northward transport of water and sediment in the past.
- Near-contemporary gullies were observed with an uncertain origin.
- Volcanism may have persisted into the last 10-15% of the planet’s history.
- The planetary dichotomy was found to be a geophysical feature with the northern hemisphere being a locus of high heat flow early in Mars’ history.
- The planet’s magnetic field appeared to cease operation early in geologic time.

2001 Mars Odyssey orbiter

- Identified hydrogen-rich layers in the subsurface, many of which correlate with regions of predicted ice stability.
- The high albedo dust covering much of Mars was found to be a thin drape of material on the order of tens of centimetres, Mars has very little exposed bedrock.
- Chlorine was found to be more enriched at the surface than previously predicted and was deposited heterogeneously. Surface materials appear to be enriched in chlorine, potassium and thorium relative to bedrock suggesting aqueous processing under low pH conditions.
- Global compositional differences suggest large scale surface chemical and mechanical processing and the presence of sinks such as fractures and depressions.
- Sulfur is distributed unevenly, with a global average concentration of 1.76% and is correlated with hydrogen suggesting abundant hydrated sulfates present on the surface.
- Thermal measurements detected no endogenic heat sources but did provide much improved imaging of volcanic features such as fissure and flank vents and lava shields.
- Interactions between lava flows and fluvial valleys indicate long periods of water release and valley formation in volcanic areas.

2003 Mars Express orbiter

- Present-day surface water is trapped in two sinks, ice in the polar caps and hydrated minerals.
- Observed iron-bearing silicates, hydrated phyllosilicates and sulfates but no carbonates.
- Mineral mapping established a mineralogical history from ancient clay forming times in the phyllosian, a transition to sulfate forming times in the theiikan and then to anhydrous ferric oxides formation in the siderikan.
- High-albedo regions contain oxidised minerals but lack hydrated signatures and are mostly dominated by nanocrystalline red haematite or maghemite, which do not require liquid water to form.
- Phyllosilicates are typically iron-rich smectites or aluminium-rich montmorillonite that form a bulk component in many ancient rocks and originated from prolonged water contact.
- Extensive sulfate deposits are inferred to have formed in the late Noachian and early Hesperian with sulfur supplied by volcanism. Sulfates do not require the long term presence of liquid water. At least two distinct climatic episodes on Mars are indicated by the stratigraphically separated phyllosilicates and sulfates.
- Detected variable levels of atmospheric methane.
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2004 Mars Exploration Rovers: Spirit and Opportunity

- Soils were of a similar composition to Viking and Pathfinder soils.
- Discovered evidence of modification by aqueous fluids during or after emplacement.
- Spirit discovered outcrops rich in magnesium-iron carbonate of debatable origin at its Gusev Crater study site.
- Spirit also uncovered bright ferric sulfate rich deposits with its wheels.
- Opportunity discovered aeolian sandstones composed of siliciclastics and sulfates including calcium and magnesium sulfates and jarosite. Jarosite is indicative of acidic waters being present at the time of its formation in the study area at Meridiani Planum.
- Rounded haematite concentrations, resulting from aqueous alteration, formed a surface lag at Meridiani.
- The precise origin of the sulfate- and iron-oxide-rich Meridiani deposits is uncertain but aqueous processes involving volcanism, ice or evaporite formation are possible.
- Some regions in Meridiani hosted only gypsum indicating some diversity in aqueous chemistry. However, most areas were similar suggesting water induced alteration at Meridiani Planum was regional in scope.

2006 Mars Reconnaissance Orbiter

- Clays are widespread in Noachian terrains, though their formation may well have been through subsurface processes, meaning long duration warm wet conditions at the surface may not necessarily have existed on ancient Mars.
- Large craters in the northern plains reveal phyllosilicate assemblages indistinguishable from the southern highlands indicating liquid water once altered both hemispheres of Mars.
- Identified several carbonate deposits that suggest the presence of ancient layered carbonates that are mostly buried.
- Observed opaline silica, mono and polyhydrated sulfates, jarosite, goethite and ferrihydrite, with sulfates, overlying Noachian clays.
- Valles Marineris shows abundant sulfates of similar composition to Meridiani Planum.
- Fractures around Valles Marineris have been cemented and bleached by fluid alteration, indicating fluid movement aided by fractures.
- The martian surface appears to have been hyperarid except during the late Noachian when episodic floods incised the numerous valleys networks.
- Many areas of Mars are too mantled in surficial materials to allow metre-scale features to be discerned.
- Impacts have frequently hit volatile-rich target areas and excavated altered crust from depth.
- Regions that may have hosted lakes or deltas would be potential sites of organic compound concentration. However, much of Mars’ early geological record is buried so ancient rocks exposed by erosion or impacts are key targets.
- Substantial glaciation occurred at the dichotomy between the northern plains and southern highlands up to the late Amazonian.
- A subsurface deposit of carbon dioxide ice was found near the South Pole.
Chapter 1 – A review of the geology and exploration of Mars

2008 Phoenix lander

- Found a shallow ice table 5-18 cm under the surface at the landing site near the North Pole.
- Mars’ soils were found to contain perchlorate salts (ClO₄⁻).
- Other ions included magnesium, sodium, potassium, calcium, chloride, bicarbonate and sulfate.
- Perchlorates released oxygen during evolved gas analysis and no organic compounds were detected, though carbon dioxide was possibly indicative of the oxidation of carbon compounds.
- Sulfate at the landing site appeared to be predominantly calcium sulfate, sulfur was at a lower concentration than at either Gusev Crater or Meridiani Planum.
- Perchlorate is inferred to form through atmospheric processes and be globally spread, its presence may allow liquid brines to temporarily exist at the very low surface temperatures on Mars.

2012 Mars Science Laboratory: Curiosity rover

- Soils in Curiosity’s landing site at Gale Crater are similar to those analysed at other landing sites.
- Evolved gas analysis of windblown soil evolved water, carbon dioxide, oxygen and sulfur dioxide suggesting perchlorates, hydrated minerals, carbonates, sulfides and sulfates.
- Oxidation of organic matter could explain some of the carbon dioxide and chlorinated hydrocarbons that were detected in the soil.
- The derivatization agent on board the rover was found in blanks indicating some had leaked despite the storage cups being sealed.
- The rover found rounded pebbles that appeared to have been modified by fluvial processes.
- A mudstone at Yellowknife Bay was found to exhibit magnetite enrichment, olivine depletion and clay minerals that formed by aqueous alteration at circumneutral pH levels for a hundreds to tens of thousands of years.
- One of the drilled samples at Yellowknife Bay, Cumberland, contained nitrates, chlorobenzene and dichloroalkanes significantly above blank levels and other samples. Some of these chlorinated hydrocarbons are inferred to be the result of chlorination of martian or exogenous organic matter and cannot be fully explained by contamination.
- These mudstone deposits were not visible from orbit due to being mantled by dust.
- The rover detected methane at low background levels and a temporary high value.
- Radiation measurements indicate recently exposed rocks would be the best prospect for organic molecule detection.
- Drilling at the base of Mount Sharp (Gale Crater’s central peak) found deposits containing jarosite that gave unusual oxygen and carbon dioxide peaks during heating that have yet to be fully explained.
Chapter 1 – A review of the geology and exploration of Mars

1.5 The current understanding of Mars

Four decades of Mars exploration has greatly improved the understanding of the geological history of the planet but diagnostic organic compounds that would inform about the historical and present day carbon cycles remain elusive (Klein, 1979; Ming et al., 2009; Glavin et al., 2013; Leshin et al., 2013). Abundant fluvial landforms in ancient terrains and clays indicative of neutral-benign waters suggest ancient Mars could have supported life (Bibring et al., 2006; Ehlmann et al., 2011; Grotzinger et al., 2015). Though the present day surface is arid water is still present in other reservoirs, such as the polar ice, hydrated minerals and subsurface ice (Bibring et al., 2005; Smith et al., 2009). Volcanism, which would have yielded abundant volatiles, heat and mobilised water has been active for most of Mars’s history (Hartmann, 1999). The question of ancient Mars’ habitability has largely been answered, the question of whether these habitable habitats were ever inhabited remains.

Perchlorates are a significant problem for the operation of thermal extraction experiments searching for organic compounds on Mars (Ming et al., 2009). Perchlorates appear to be globally spread and decompose at relatively low temperatures and in the process release chlorine and oxygen that will oxidise and chlorinate organic matter, potentially rendering organic matter undetectable (Archer et al., 2013; Glavin et al., 2013). Recent in-situ experiments by Curiosity suggest that some organic matter is preserved on Mars but it remains the case that thermal extraction has so far only detected simple chlorinated hydrocarbons of ambiguous origin, with perchlorate decomposition a contributing factor (Freissinet et al., 2015b; Grotzinger et al., 2015; Stern et al., 2015). However, perchlorate formation may be a relatively recent phenomenon and some ancient rocks extracted from depth may be perchlorate poor or free (Hecht et al., 2009). It is important to consider if any
other minerals have a detrimental effect on thermal extraction. This PhD thesis considers the influence of sulfate minerals as they are salts containing oxygen, like perchlorate. Sulfur is known to be a component of both bedrock and the apparently globally spread dust layer (Baird et al., 1976; Golombek et al., 1997a; Bibring et al., 2006; Squyres et al., 2006; Milliken et al., 2008; Hecht et al., 2009; Arvidson et al., 2010; McLennan et al., 2010; Leshin et al., 2013; Rampe et al., 2015). Many different forms of sulfate have been detected, with a peak period of sulfate formation in the late Noachian and Hesperian due to volcanic outgassing (Bibring et al., 2006). Noachian terrains make up 40% of the martian surface, Hesperian terrains 34% and Amazonian 26% (Croswell, 2003). If sulfate minerals prove to also be problematic to organic compound detection through thermal extraction then at least a third of the planet could pose not only a perchlorate problem but also a ‘sulfate setback’.

![Image](image.png)

Figure 1.38. As Curiosity begins to collect and analyse data at the sulfate bearing base of Mount Sharp it is important to consider whether these oxygen and sulfur containing salts could pose a problem for thermal extraction experiments on top of that created by perchlorates (Freissinet et al., 2015b).
Chapter 2 - Field work and methodology
Mars global image from NASA/JPL-Caltech (2013)
2.1 Introduction

To assess the influence of sulfate minerals on thermal extraction experiments a range of natural samples, laboratory standards and synthetic samples were obtained. It was decided to focus research on the mineral jarosite ($\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$), which has been observed at several locations on Mars (Squyres et al., 2004; Squyres et al., 2006; Milliken et al., 2008; Rampe et al., 2015), is indicative of potentially habitable environments (Arvidson et al., 2010), and iron sulfates are known to break down at relatively low temperatures (Frost et al., 2005a). Jarosite group minerals generally form as a secondary phase in the weathered zones of sulfide rich regions and precipitate in low pH waters (Desborough et al., 2010). The formation of jarosite can also be microbially mediated by the action of organisms such as sulfur and iron oxidising bacteria (Sasaki et al., 2006). However, jarosite only persists for geological time scales in arid regions as in the continued presence of water it rapidly decomposes into ferric oxyhydroxides (Elwood-Madden et al., 2004).

Jarosite has been observed at several sites already used for astrobiological studies, such as Río Tinto in Spain and the Panoche Valley in California (Navarro-González et al., 2006), but it is also present at many locations in the United Kingdom. The decision to focus on jarosite turned out to be particularly timely with Curiosity’s discovery of jarosite at the base of Mount Sharp in Gale Crater in 2015 (Map 3) (Rampe et al., 2015).
2.2 Sampling

Natural samples were obtained through field work at several sites across the United Kingdom. In 2012 fieldwork was conducted at Brownsea Island and St. Oswald’s Bay in Dorset. In 2013 the tailings of a baryte/lead mine in the Lake District were sampled for lead jarosite (plumbojarosite) and additional work was performed in St. Oswald's Bay with a study of a sulfate rich stream discovered in the east of the bay.

These sampling sites yielded different varieties of jarosite (such as potassium-rich jarosite and sodium-rich jarosite), as described fully in Chapters 3-6 (the data chapters). The diversity of the samples allowed a broad range of studies to be conducted. The field sites and materials collected are described in detail in this chapter. To augment the interpretation of the decomposition of complex natural samples two forms of jarosite, potassium rich and sodium rich, were synthesised in the laboratory as described in this chapter. Synthetic samples also allowed the interaction between jarosite and organic compounds to be directly investigated without the complication of other mineral phases being present.

Sample preparation techniques and laboratory methods and instruments are described in Section 2.3. Some of the temperature settings used in pyrolysis experiments and the choice of laboratory standards are described in the relevant data chapters as selection was closely linked to each project’s aims and objectives.
2.2.1 Brownsea Island

On the 11th October 2012 jarosite sampling was conducted at Brownsea Island, Dorset, UK (Figure 2.1). The Island was selected as a study site as it was identified as a location hosting jarosite on the website mindat.org and was described and photographed in detail by Professor Ian West on his website describing Dorset geology (West, 2013). 2012 was an exceptionally wet year and it was a concern that jarosite present on the cliffs of the island may have been washed out or decomposed to iron oxide. However, the chance of finding jarosite outcrops on Brownsea was increased by the island’s stratigraphy, which consists of subhorizontal beds meaning the lignite and pyrite bearing Parkstone Clay member is almost
continuously exposed along the southern coast (West, 2013). It is the pyrite within the Parkstone Clay that oxidises to jarosite when it reaches the near surface (West, 2013).

Brownsea is owned and managed by the National Trust, who granted permission to work on the island. It was raining on the day of fieldwork, which dulled the colour of the cliff faces making it somewhat difficult to differentiate jarosite from the rock faces it was growing on. Having traversed from east to west along the coast, the first sampling was made on the west of the bay where a very thin yellow-brown veneer could be seen on the grey clay (Figure 2.2). The clay was very wet and easy to remove from the cliff using the sharp end of a hammer. Within the clay were dark patches of lignite and very weathered gold-brown iron-rich concentrations about 0.5-1 cm across that broke apart easily.

In photographs taken in earlier years by Professor West jarosite was present on the Brownsea Cliffs as bright yellow thick crystalline growths (West, 2013). The outcrops observed in this field work were instead a dull yellow-orange that formed amorphous looking plates on the
cliff faces, these observations guided the remainder of the field work as well as showing the susceptibility of jarosite to further aqueous alteration in wet environments. Eventually towards the centre of the southern coast a much better outcrop was found in a cliff section that was overhung by vegetation, which presumably created a somewhat drier environment (Figure 2.3).

The jarosite deposits at this locality were noticeably more yellow and significantly thicker though they still appeared to be poorly crystalline. Fine laminations were discernible in the Parkstone Clay and dark patches of lignite were much more obvious. At the base of the cliff was a hard rusty layer that was interpreted to form as jarosite slumps down the cliff face and oxidises to iron oxide. Samples were removed from cliff faces with a hammer, wrapped in foil, labelled and placed in a sealed plastic bag. The samples were dried out on a lab bench at room temperature to prevent any decomposition of the jarosite into iron oxides (Figure 2.4).

![Figure 2.3. Much thicker jarosite outcrops were found in a sheltered section of the cliff with overhanging soils and vegetation. At the base of the cliff was a hard iron oxide layer.](image)

The jarosite deposits at this locality were noticeably more yellow and significantly thicker though they still appeared to be poorly crystalline. Fine laminations were discernible in the Parkstone Clay and dark patches of lignite were much more obvious. At the base of the cliff was a hard rusty layer that was interpreted to form as jarosite slumps down the cliff face and oxidises to iron oxide. Samples were removed from cliff faces with a hammer, wrapped in foil, labelled and placed in a sealed plastic bag. The samples were dried out on a lab bench at room temperature to prevent any decomposition of the jarosite into iron oxides (Figure 2.4).

![Figure 2.4. Hand samples from Brownsea, left: clay with a thin jarosite crust, right: clay with a thick jarosite crust.](image)
2.2.2 St. Oswald’s Bay

On the 13th October 2012 further fieldwork was conducted in the Dorset area at St. Oswald’s Bay (Figure 2.5). Unlike Brownsea Island the beds in St. Oswald’s Bay are subvertical. The bay hosts clay beds that contain pyrite and it was hoped that the high degree of lateral variation would mean that different types of jarosite would be growing on different cliff faces. A traverse of the bay from west to east was undertaken and three different environments in which jarosite was forming were encountered.

Figure 2.5. The location and geological setting of the Jurassic and Cretaceous beds within St. Oswald’s Bay and the Lulworth area, geological map and cross section adapted from House (1993).
The subvertical beds in the bay are due to a structure known as the Purbeck Monocline, which formed by folding associated with the reactivation of a reversed normal fault in the early Cenozoic (House, 1993). The pyrite-bearing and clay-rich Wealden group is one of the first units encountered after descending into the bay via the stairs from Durdle Door (Kemp et al., 2012). Yellow and rusty stains can be seen all over the surface of the Wealden and the beds are overturned and dipping south. In the exposure by the stairs a sequence of three thin beds was studied (Figure 2.6). At the base of the sequence is a light-coloured clay capped with a thin layer of yellow jarosite clay, the clay stratigraphically above this is darker in colour and contains a patchy bed of lignite and then a more continuous layer of iron oxide.

The next locality was a decomposed pyrite nodule located on a cliff face in the pyrite-bearing Gault and Greensand stratigraphically on top of the Wealden (Figure 2.7) (Toghill, 2012).
Chapter 2 – Field work and methodology

The eastern end of the bay curves back into the Wealden and at this location many of the light boulders eroded from the cliffs can be seen to be coated with iron concretions suggesting acidic iron-rich waters in the vicinity. The source was found to be waters flowing out of slumped Wealden beds a short distance from the beach in a small stream in which jarosite was precipitating and partially decomposing to iron oxide (Figure 2.8). A purple coloured microbial mat could be seen to frequently coat the iron oxide and moss was often present on the thicker iron oxide crusts suggesting a distinct ecological system was being supported in this acidic sulfur-rich environment.

Figure 2.8. Acidic sulfur rich waters flowing out of slumped Wealden beds. These waters precipitate jarosite. An ecological system appears to be present here that is distinct from the surrounding grassy slopes. The stream can be seen flowing parallel to the grassy banks on the left of the photo. On return to this site in 2013 the stream had switched its location to the other side of the jarosite and iron oxide encrusted area.
The rusty crust was cut through with a metal ruler and a thin jarosite layer could be seen underneath, the jarosite and iron oxide layers were sampled (Figure 2.9).

This small stream was named as Pequeño Río Tinto (PRT) and was the most significant locality sampled in St. Oswald’s Bay. The other localities in the Bay and at Brownsea Island were nodules and concretions that are of mineralogical interest. PRT is also of mineralogical interest but in addition it hosts a small ecosystem supported by acidic sulfur rich waters. If such a system existed in the distant past on Mars the mineralogical record it may have left behind may be very similar to what is observed at PRT. With this in mind a much more rigorous sampling of PRT was conducted a year later and is described in Section 2.2.4.
2.2.3 Sandbed Mine, Lake District

On the 31st July 2013 fieldwork was conducted in the tailing dams of an old mine in the northeast of the Lake District, Cumbria (Figure 2.10). The Sandbed Mine is located in the Caldbeck Fells and was listed on mindat.org as a location at which lead jarosite (plumbojarosite) could be found. The mine ceased operation in 1966 and was the site of zinc, lead, copper and iron mining (Tyler, 2009). It was hoped that lead jarosite would be growing on the dumped material outside of the mine. Obtaining lead jarosite would allow the influence of different cations on jarosite decomposition to be assessed.

Mineral sampling in the Lake District is strictly controlled by the Lake District National Park Authority. A green pass was granted, which permitted sampling to take place at Sandbed Mine. Unfortunately sampling is prohibited to all at the nearby Roughton Gill mine, which would have been the best prospect for locating good lead jarosite outcrops.
Chapter 2 – Field work and methodology

The mine was reached by a path leading south from Calebreck Farm, two mine dumps could be seen, the lower mine dump was smaller and had a distinct orange tint at its most northern end, the larger mine dump was located further up the hill (Figure 2.11).

![Image](image.png)

Figure 2.11. Sandbed Mine viewed looking south onto the Calbeck Fells. Insets show a closer view of the two mine dumps.

The material at both sites was heavily weathered and broke apart easily during handling. Quartz veins up to 2-3 cm across cross cut the specimens frequently. Though the quartz was generally well crystallised, the veins fragmented easily. A common feature across both mine dumps was a very fine grained orange-brown material surrounding the clear to white quartz veins. Samples exhibiting the distinct yellow of some of the jarosite specimens seen at Brownsea Island and St. Oswald's Bay were not seen. The difference may be attributed to the relative dryness of this location and the jarosite, if present, was likely to be relatively old and starting to decompose to an iron oxide. The orange-brown material and veins were sampled in the hope that there may be some jarosite within the finer material. The veins in the lower mine dump material typically contained some darker crystals that were too small to identify.
in the field. Most of the veins at the upper mine dump were more clear, other than a few which showed similar small dark crystals and distinct green-turquoise crystals (Figure 2.12).
2.2.4 A sulfate ecosystem: Pequeño Río Tinto

2.2.4.1 Introduction to the study area

On the 12\textsuperscript{th} October 2013 further sampling was carried out at the sulfate rich stream in St. Oswald’s Bay, Dorset. A series of samples were taken across the study area using a trowel to cut cores that were approximately 10 cm in diameter and around 10-15 cm in depth. On the 13\textsuperscript{th} October an additional core was taken from nearby Stair Hole that appeared to be a similar system that had dried out (Figure 2.5). The St. Oswald’s Bay stream had a pH of approximately 3.5 but was biologically active as it bubbled when exposed to direct sunlight and contained abundant green matter (Figure 2.13). In addition to the cores, the water and green material were sampled and stored in bottles. Yellow crystals that were found growing on woody materials near core 8 were also sampled. Individual layers of jarosite clay, the rusty crust, the microbial mat and clay in the surrounding grassland were collected and stored in centrifuge tubes. As seen in Figure 2.14 there was significant lateral variation across the 4 m study area. The stream was found to be flowing along a different channel (on the western side of the system) than was observed in 2012 (Figure 2.8) suggesting intermittent flows or migration.

Figure 2.13. The sulfate ecosystem in St. Oswald’s Bay is characterised by a vertically and horizontally highly variable environment. The abundant green matter within the pH 3.5 stream can be clearly seen in this photo and bubbles that were released when the sun was shining on the water can be seen behind the pH strip.
Figure 2.14. Cores taken from across the sulfate stream are labelled 1-9, an additional core was taken from nearby Stair Hole where a similar system appeared to have dried out.
2.2.4.2 Sampling overview

Core 1 was taken from a sandy-clay in which grass was growing. Cores 2-6 had a general lithology of sandy-clay capped with jarosite topped by a rusty crust with a fibrous purple microbial mat growing on it, with occasional moss and grass (Table 2.1). To the western side of the stream (Figure 2.14), localities 7-9 were much drier and displayed predominantly sandy-clays but jarosite appeared to be a major phase and yellow crystals were seen growing on surfaces, particularly on woody material contained in the unit (Figure 2.15).

Table 2.1 Materials collected at the sulfate stream and Stair Hole.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Core/Location</th>
<th>Description of vial contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>1G</td>
<td>1</td>
<td>Grass covering the top of core 1</td>
</tr>
<tr>
<td>1C</td>
<td>1</td>
<td>Sandy-clay</td>
</tr>
<tr>
<td>2W</td>
<td>2</td>
<td>Wood fragments</td>
</tr>
<tr>
<td>2C</td>
<td>2</td>
<td>Jarosite clay</td>
</tr>
<tr>
<td>3M</td>
<td>3</td>
<td>Microbial mat</td>
</tr>
<tr>
<td>3R</td>
<td></td>
<td>Rusty crust</td>
</tr>
<tr>
<td>3C</td>
<td></td>
<td>Jarosite clay</td>
</tr>
<tr>
<td>4M</td>
<td>4</td>
<td>Microbial mat</td>
</tr>
<tr>
<td>4R</td>
<td></td>
<td>Rusty Crust</td>
</tr>
<tr>
<td>4C</td>
<td></td>
<td>Jarosite Clay</td>
</tr>
<tr>
<td>5W</td>
<td>5</td>
<td>Wood fragments</td>
</tr>
<tr>
<td>5R</td>
<td></td>
<td>Rusty Crust</td>
</tr>
<tr>
<td>5CT</td>
<td></td>
<td>Clay top</td>
</tr>
<tr>
<td>5CB</td>
<td></td>
<td>Clay base</td>
</tr>
<tr>
<td>6N</td>
<td>6</td>
<td>Example of nodule edge</td>
</tr>
<tr>
<td>6E</td>
<td></td>
<td>Exterior of nodule (moss and possibly mat)</td>
</tr>
<tr>
<td>6I</td>
<td></td>
<td>Interior of nodule</td>
</tr>
<tr>
<td>6C</td>
<td></td>
<td>Jarosite clay</td>
</tr>
<tr>
<td>7W</td>
<td>7</td>
<td>Wood fragments</td>
</tr>
<tr>
<td>7C</td>
<td></td>
<td>Jarosite and iron oxide clay</td>
</tr>
<tr>
<td>7J</td>
<td></td>
<td>Jarosite rich sub layer</td>
</tr>
<tr>
<td>8CT</td>
<td>8</td>
<td>Clay top (above wood)</td>
</tr>
<tr>
<td>8W</td>
<td></td>
<td>Wood</td>
</tr>
<tr>
<td>8J</td>
<td></td>
<td>Jarosite nodule</td>
</tr>
<tr>
<td>8WJ</td>
<td></td>
<td>Material immediately surrounding jarosite nodule</td>
</tr>
<tr>
<td>8CB</td>
<td></td>
<td>Clay base (below wood)</td>
</tr>
<tr>
<td>9C</td>
<td>9</td>
<td>Clay</td>
</tr>
<tr>
<td>SHM</td>
<td>Stair Hole</td>
<td>Microbial mat</td>
</tr>
<tr>
<td>SHJT</td>
<td></td>
<td>Jarosite at top of core</td>
</tr>
<tr>
<td>SHR</td>
<td></td>
<td>Rusty material that makes up most of the core</td>
</tr>
<tr>
<td>SHJB</td>
<td></td>
<td>Jarosite at the base of the core</td>
</tr>
<tr>
<td>AC</td>
<td>Core 1</td>
<td>Clay isolated layer</td>
</tr>
<tr>
<td>AR</td>
<td>Between cores 5&amp;6</td>
<td>Rust isolated layer</td>
</tr>
<tr>
<td>AJ</td>
<td>Core 3 hole</td>
<td>Jarosite isolated layer</td>
</tr>
<tr>
<td>AM</td>
<td>Between cores 4&amp;5</td>
<td>Microbial Mat isolated layer</td>
</tr>
<tr>
<td>JWN</td>
<td>Between cores 8&amp;9</td>
<td>Example of yellow crystals growing on wood</td>
</tr>
<tr>
<td>JW</td>
<td>Between cores 8&amp;9</td>
<td>Yellow crystals that were growing on wood</td>
</tr>
<tr>
<td>W</td>
<td>Between cores 8&amp;9</td>
<td>Wood</td>
</tr>
<tr>
<td>SG</td>
<td>Stream</td>
<td>Stream water and green matter</td>
</tr>
<tr>
<td>SC</td>
<td></td>
<td>Clear stream water</td>
</tr>
</tbody>
</table>
The isolated layers were sampled where there was good exposure of the main compositional endmembers; clay, jarosite, iron oxide and the microbial mat. These were collected as back up samples to the cores. Water was sampled in two plastic bottles, with one containing just water and the other water with the green biological matter. The Stair Hole site appeared similar to PRT but only a very weak clear stream with a pH of 5 was seen and the system seemed to have largely dried out. A dark coloured fibrous microbial mat covered much of the surface with some earthy orange and dark red brown layers underneath. A single core was taken through the centre of the unit. The samples were wrapped in foil and stored in labelled plastic bags. In the laboratory, the collected materials were dried out on a lab bench before being frozen. In December 2014 a saw was used to cut the samples in half and then to separate out any layers seen within each core.

Figure 2.15. This photo shows the main components of the sulfate ecosystem during sampling. In the foreground is clay with a yellow tint due to the presence of jarosite. Beyond the small stream is a hard rusty crust with coverings of moss. There is also a purple microbial mat, which has a distinctive surface sheen.
2.2.4.3 Core 1

Core 1 is made up of a relatively homogenous sandy-clay but it does appear to contain some jarosite (Figure 2.16). The surface of the core is capped with grass. The grass was added to a separate vial and the clay into another. Ideally the clay would have been separated into a top layer and a bottom layer as the jarosite seemed to occur primarily at depth. However, as the cores were prepared in reverse order this was the last sample to be divided into layers and the saw used to cut the frozen cores had been damaged by earlier cutting and was unable to cut the frozen clay properly.

Figure 2.16. The sampling of core 1. A: The trowel is embedded in the ground at the location where the core was extracted from the grassy clay at the edge of the sample site. B: The extracted core is shown on foil immediately after extraction. C: The frozen core before cutting. D: Vials containing separate portions of the clay and grass.
2.2.4.4 Core 2

Core 2 consists of a sandy jarosite containing clay where jarosite is found mainly concentrated on the upper surface of the core (Figure 2.17). Some wood fragments were also found near the top of the core, which were isolated into a separate vial, jarosite was growing readily on this wood. This area was cored as it was the location of the first significant coatings of jarosite seen at the surface at the transition between the grass hosting clay and the acidic stream.

Figure 2.17. The sampling of core 2. A: The cut made by the trowel can be seen at the transition between the grassy clay and the oxidised surface richer in jarosite towards the base of the photo. B: The extracted core on foil at the sampling site. C: The frozen core, the jarosite enrichment can be clearly seen at the top of the core. D: The vials containing the sandy jarosite clay and the wood fragments with a coating of jarosite.
2.2.4.5 Core 3

Core 3 is capped with a fibrous microbial mat covering a layer of iron oxide that separated from the sandy-clay underneath during core extraction (Figure 2.18). The mat was scraped off and placed into a vial and the iron oxide underneath was placed into another vial. The sandy jarosite clay layer appeared homogenous and was placed in a third vial.

Figure 2.18. The sampling of core 3. A: The clear layering in this section can be seen in the hole left by core extraction, a clay containing abundant jarosite is capped with a thin iron oxide layer and a slightly thicker purple fibrous microbial mat with a distinctive sheen. B: The extracted core. C: The frozen core, the mat and iron oxide can be seen separated from the homogenous jarosite-rich clay. D: The three vials containing the microbial mat, iron oxide and jarosite clay.
2.2.4.6 Core 4

Core 4 was somewhat poorly consolidated and fragmented whilst being transported. Despite sample friability in the frozen material a soft cap could still be discerned at the top of the core, with a rusty layer below and a homogenous sandy jarosite-rich clay underneath (Figure 2.19).

Core 4 is very similar to core 3.

Figure 2.19. The sampling of core 4. A: The trowel is seen stuck in the waterlogged material in the centre of the study area. The hole left from the sampling of core 3 can be seen in the top right. B: The frozen material from core 4 had broken up during transport but the microbial mat, rusty layer and jarosite-rich sandy-clay could still be isolated. C: The isolated layers from core 4 in their respective vials.
2.2.4.7 Core 5

When core 5 was extracted from the ground there was a strong smell of hydrogen sulfide and a thin green layer was seen at depth in the core that was interpreted to possibly be reduced iron. The oxidising conditions at the surface appear to not extend far into the waterlogged clay. In the frozen core the mat and iron oxide were not thick enough to be separated so were sampled as one layer. The green layer at the base of the core was not present after a year of storage, despite being dried out and frozen following collection and before storage. The base of the core was a sandy material with occasional yellow patches so this was sampled separately to the clay immediately beneath the iron oxide. Wood fragments found were isolated in a separate vial (Figure 2.20).

Figure 2.20. The sampling of core 5. A: The core was cut where the iron oxide crust was relatively thin near to the small stream filled with green biological matter. B: A strong smell of hydrogen sulfide indicated that core extraction had exposed a reducing environment. C: The reduced green iron layer had vanished during storage over a year. D: The vials from the different components of core 5.
2.2.4.8 Core 6

Core 6 was capped with moss that was growing on a hard iron oxide nodule on top of the usual homogenous jarosite clay (Figure 2.21). When the frozen core was cut in half it was found that the moss had been compacted making it difficult to separate from the iron oxide crust. When the nodule was cut in half it was found that the core consisted primarily of sandy material surrounded by a very thin jarosite layer that was then capped with the iron oxide and moss.

Figure 2.21. The sampling of core 6. A: The core was capped with a tough iron oxide layer and moss. B: The top was tough and stuck together but the underlying clay immediately crumbled after extracting the core. C: The sandy core of the nodule can be seen along with the thin yellow jarosite layer capped with iron oxide and moss. D: The four vials that contain the materials sampled from core 6.
2.2.4.9 Core 7

Core 7 was extracted from the soils immediately to the west of the small acidic stream running through the centre of the study area. The ground was noticeably drier and harder to dig and when the core was removed, repeated layers of yellow jarosite clay and dark iron oxide could be seen. This layering combined with the observation the stream was in a different location in 2013 relative to 2012 suggests that transient acidic waters repeatedly deposit jarosite, which then decomposes on the immediate surface to iron oxides. Frustratingly the core did not store well and the layering became indistinct. An average composition was sampled along with a brighter more jarosite-rich region. Wood fragments were also found and isolated (Figure 2.22).

Figure 2.22. The sampling of core 7. A: The core was cut from dry soils immediately to the west of the acidic stream. B: Repeated light and dark layers could be seen in the soils. C: The core was not cohesive and crumbled during storage. D: Wooden fragments, an average of the core mineralogy and a jarosite-rich layer were isolated into vials.
2.2.4.10 Core 8

Core 8 was collected further from the centre of the stream and the layering seen in core 7 disappeared. When the frozen core was cut in half, the sandy-clay appeared homogenous other than a wood layer bisecting the core horizontally. This layer was then sliced through horizontally and a small jarosite nodule about 2 cm across was found growing in this material. The clay above and below the wood was sampled as well as the jarosite nodule, the material immediately surrounding it, and the wood layer as a whole (Figure 2.23).

![Image]

Figure 2.23. The sampling of core 8. A: The core was cut from dry sandy material further from the acidic stream than core 7. This material contained lots of wood fragments, in the top right of the photo the wood upon which yellow crystals were found growing (described in 2.2.4.12). B: When cut in half a woody layer was seen bisecting the core. C: When this layer was sliced horizontally a bright yellow jarosite nodule was found. D: The samples taken from core 8 were the sandy-clay above the wood, the jarosite nodule, the material immediately surrounding the nodule, the wooden layer as a whole and the clay beneath the wood.
2.2.4.11 Core 9

Core 9 was a very homogenous sandy jarosite clay, so the material was added to one vial (Figure 2.24).

![Figure 2.24. Sampling of core 9. A: The material in this area was dry, sandy and poorly cohesive. B: When cut in half the core was very homogenous with depth. C: The core material was sampled in one vial.](image)

2.2.4.12 Jarosite growing on wood

Close to core 8 yellow crystals that were interpreted to be jarosite were found growing on wood (Figure 2.25).

![Figure 2.25. Distinct yellow crystals are observed growing on wood fragments in the sandy layer. B: The crystals, the wood they were growing on and crystal encrusted wood were sampled.](image)
2.2.4.13 Stair Hole

The Stair Hole system appeared to have largely dried out and was very difficult to cut into with the trowel. A small stream could be seen but with a weaker flow than that seen in St. Oswald’s Bay, there was no green biological matter though there was a sheen to the water suggesting some sort of biological activity. The pH of the water was 5. When the frozen core was cut in half, a mat like material separated from the top so this was sampled and placed in a vial (Figure 2.26). A light yellow material was seen immediately beneath the mat, most of the core was an orange-red material but there was a second light yellow layer at depth. The material appeared much richer in iron oxide than any of the cores sampled at St. Oswald’s Bay.

Figure 2.26. A: The stream at Stair Hole is much weaker than that seen at St. Oswald’s Bay and has a pH of 5 but it does have a surface sheen. B: A core was taken from the centre of the dried out system. C. The frozen core cut in half, the mat like material at the top separated from the core. D: The mat material, two separate jarosite-rich layers and the overall core were sampled into vials.
2.3 Laboratory techniques

2.3.1 Introduction and sample preparation

As jarosite decomposes in the continued presence of water to ferric oxides it was important to make sure that collected samples were dry before storage. It was also necessary to crush the samples into fine powders to permit X-ray diffraction (XRD) and pyrolysis experiments.

2.3.1.1 Sample drying

The majority of samples were left on a lab bench to dry out before being stored, the exceptions were the individual layers and water samples collected from PRT, which were frozen without drying to preserve the samples exactly as they were upon collection. The cores collected from PRT were frozen after bench drying until the experiments were ready to begin in case any water remained within the cores. After the frozen cores had been divided and cut and the individual layers collected into vials they were dried out completely using a Labconco freeze dryer, which uses low temperatures and pressures to drive off water.

2.3.1.2 Sample grinding

The first attempt at sample grinding and homogenisation was performed on the materials collected at Brownsea Island. A Tema mill was used to crush the hand specimens. The soft jarosite was found to adhere to surfaces very strongly and it was difficult to remove from the instrument. The adhered jarosite was removed most effectively by using dilute hydrochloric acid. An agate pestle and mortar was used to prepare the remainder of the samples. Agate was a preferred material relative to ceramics as it scratched less easily meaning jarosite was significantly easier to remove from the mortar after grinding. Jarosite could usually be removed by grinding with a mixture of water and sand without the need for acid treatment.
2.3.2 Synthesis of jarosite

Potassium and sodium jarosite were synthesised using a method adapted from that described by Basciano & Peterson (2008). The mass of standards used was adjusted to the volume of the reaction chamber, which was a 75 ml stainless steel Parr pressure vessel. 18 g of ferric sulfate hydrate was mixed with 0.3825 g of either potassium or sodium sulfate and then 45 ml of deionised water (Figure 2.27). The vessel was sealed and heated at 140 °C in a furnace for 192 hours. The headspace was not purged to ensure the system contained abundant oxygen. It should be noted that corrosion of the vessel was observed after synthesis, particularly at the interface between water and the headspace of the vessel. The optimisation of jarosite synthesis is described in Chapter 4.

Figure 2.27. The pressure vessel setup used to synthesise jarosite. Water and sulfate standards were sealed inside the vessel, which was then placed inside a heating jacket. Temperature and pressure could be monitored throughout the experiment using the large pressure gauge on top of the vessel and the digital readout on the heater controller.
2.3.3 X-ray diffraction

XRD identifies crystal phases by investigating how X-rays diffract through the atomic structure of crystals. An X-ray source is aimed at the target sample at an angle (Θ) with the X-ray detector positioned opposite at an angle of 2Θ to the incident ray. The sample is rotated so the angle to the incident ray varies, at certain angles X-rays diffracted through the crystal lattice will constructively interfere and produce a spike in X-ray intensity measured by the detector. Different crystal lattices produce characteristic spikes in diffracted X-ray intensities at particular angles and the diffraction pattern produced from a crystalline mixture can be used to interpret the phases present within the material using a reference database of phase peaks. As the Brownsea and Lake District materials, and the samples collected from St. Oswald’s Bay in 2012, were a relatively small number of samples they could all be run manually by back loading powdered samples into a flat holder (Figure 2.28).

Figure 2.28. Powders mounted in flat holders ready for XRD analysis.
Chapter 2 – Field work and methodology

The samples were analysed within the Natural History Museum’s Panalytical X’Pert Pro Alpha-1 system (Figure 2.29). Powders were analysed between 5 and 90 °2ө for three and a half hours under copper radiation with an X’Celerator detector. The diffraction patterns were analysed with the X’Pert HighScore program with reference patterns from the International Centre for Diffraction Data’s (ICDD’s) Powder Diffraction File (PDF)-2 and (PDF)-4 databases. The X’Pert software was also used to perform Rietveld refinements, which allow quantification of crystalline phases in the sample to an accuracy of 1-3% (accuracy increases with phase abundance).

Figure 2.29. The Panalytical X’Pert Pro Alpha-1 XRD system during analysis. The flat holder is located in the stand seen through the lower middle of the right hand door.
For the series of samples collected from PRT in 2013 there were 27 mineral samples to analyse so an alternative XRD instrument available at the Natural History Museum was used that includes an autosampler. The holders were slightly larger and to reduce the risk of preferred orientation in the sample grains the materials were back loaded onto fine-grained sand paper (Figure 2.30). The instrument used was a Philips PW 1830 with the sample analysed under copper radiation between 2.5 and 90 °2θ using an angle step size of 0.02 with 2 seconds per step. 

The decision to back load powders (with loading onto a sandpaper surface for the PRT samples) was made to reduce preferred orientation in the powders, which would lead to a diffraction pattern that did not reflect the range of crystal lattices in a sample correctly. As well as identifying phases in a sample and quantifying their relative abundance, XRD also provides an estimation of the unit cell of major crystalline phases in natural samples. This is particularly useful in this project as the unit cell of jarosite (estimated through Rietveld refinement) can inform about the approximate abundance of potassium, sodium and...
hydronium in each jarosite sample (if jarosite is present at an abundance of around 5% or
greater) (Basciano & Peterson, 2008).

2.3.4 Fourier Transform Infrared (FTIR) spectroscopy
Attenuated Total Reflectance (ATR) FTIR is an extremely rapid analytical approach that uses
infrared spectroscopy to examine the chemical bonds within materials. Small amounts of
sample were loaded onto a plate made out of a diamond crystal on an in-house Nicolet 5700
FTIR spectrometer. The powder was then pressed by rotating the handle of a compactor until
the handle slips, which ensures a uniform pressure is applied to each sample analysed. An
infrared beam then passes through the surface of the sample contacting the diamond and
measures wavenumbers between 400 - 4000 cm\(^{-1}\), it takes around 30 - 60 seconds to obtain
a spectrum. Spectra were obtained and analysed using the OMNIC software package.

2.3.5 Scanning electron microscopy
As discussed in Chapter 6, the crystals growing on wood found near core 8 of PRT were found
to contain an unusual mineral phase known as metasideronatrite (Na\(_2\)Fe(SO\(_4\))\(_2\)(OH)(H\(_2\)O)). To
better characterise the elemental composition of this phase a subsample was analysed using
a LEO 1455 VP scanning electron microscope (SEM) with supervision at the Natural History
Museum.

2.3.6 Wet chemistry
Wet chemistry was used to characterise carbon in the natural jarosite clay collected from
Brownsea Island, the results are discussed in Chapter 3. Acid washing was used to determine
the amount of inorganic carbon present in the sample as carbonate while solvent extraction
was used to analyse the extractable organic matter present in the clay.
2.3.6.1 Acid washing

The natural jarosite clay was washed in 1 M hydrochloric acid. The acid was first pipetted dripwise onto the sample but no effervescence was observed so it was mixed with 10 mL of the acid. A centrifuge was used to separate the acid from the solid and it was pipetted off and replaced with fresh acid three times. The natural jarosite clay was then rinsed in deionised water until the pH returned to neutral. Samples of the untreated and acid treated natural jarosite clay were then sent to Iso-Analytical Limited for analysis by elemental analyser-isotope ratio mass spectrometry (EA-IRMS), which allowed the total carbon in the sample to be measured. The difference in total carbon between the untreated and acid-treated samples allows the ratio of organic carbon to carbonate to be assessed. The acid treated and untreated samples were also pyrolysed to compare the amount of carbon dioxide given off. Findings from EA-IRMS and pyrolysis agreed well so the inorganic vs. organic carbon content of some of the materials from St. Oswald’s Bay was estimated using acid washing combined with pyrolysis.

2.3.6.2 Solvent extraction

To examine the extractable organic matter within the sample 2 g of the natural jarosite clay was divided equally between two test tubes, and each sample was extracted with 5 mL of a 95:5 dichloromethane:methanol solvent mixture. The tubes were sonicated and then centrifuged and the supernatant was pipetted off into a third test tube. The extraction was repeated three times, with the resulting supernatants added to the third test tube. The total supernatant was evaporated under nitrogen and then stored in a vial before subsequent analysis.
2.3.7 Pyrolysis

To investigate the thermal decomposition of samples, powders were loaded into quartz pyrolysis tubes and held in place by quartz wool. The mass of sample was typically in the range of 1-10 mg, the exact masses used in each experiment are discussed in Chapters 3-6. For the works discussed in Chapters 3-5 the pyrolysis tubes were placed inside the platinum coil of a CDS 5200 pyroprobe (Figure 2.31) and then sealed under a helium flow, for the experiments discussed in Chapter 6 a CDS 2000 pyroprobe was used as the 5200 was being used on another instrument. The coil was heated at the maximum rate of 20 °C ms⁻¹ to the target temperature where it was held for 15 seconds. The interface was typically held at 150 °C (if another temperature was used it is stated in the relevant chapter) and coupled to a gas chromatograph-mass spectrometer (GC-MS) for direct injection.

![Figure 2.31. Powdered samples are loaded into quartz pyrolysis tubes and secured with quartz wool at both ends. The tube is then placed in the platinum coil of a pyroprobe, shown on the right.](image)

2.3.8 Gas chromatography-mass spectrometry

GC-MS is used to characterise the species within a gas or liquid. A coiled tube known as a gas chromatography column is used to separate out the different phases. Different species pass through the column at different rates and are associated with characteristic retention times. The mass spectrometer then measures the mass of the molecules as they leave the column.
(Figure 2.32). Different columns are used depending on experimental aims, some are designed for the separation of light gases, while others separate larger compounds typical of more complex organic molecules. The production of light gases during pyrolysis, such as carbon dioxide and sulfur dioxide, was analysed by GC-MS with an Agilent Technologies 6890 gas chromatograph coupled to a 5973 mass spectrometer. The gas chromatograph injector was held at 200 °C and operated in split mode (35:1) with a column flow rate of 2 mL min\(^{-1}\). Separation was performed on a J&W GS-Q PLOT column (30 m x 0.32 mm). The gas chromatograph oven was held for five minutes at 35 °C and then ramped at a rate of 10 °C min\(^{-1}\) to 200 °C, where it was held for 4 minutes. Mass spectra were acquired in the scan range 10-150 atomic mass units (amu). Any experimental modifications to the methods discussed in this section are outlined in the relevant chapters.

For pyrolysis experiments searching for organic compounds the gas chromatograph injector was held at 270 °C and operated in split mode (65:1) with a column flow rate of 1.1 mL min\(^{-1}\). Separation was performed on a J&W DB-5MS UI column (30 m x 0.25 mm x 0.25 µm). The gas chromatograph oven was held for 2 min at 35 °C and then ramped to 300 °C where it was held for 8 minutes. Mass spectra were acquired in the scan range 45-550 amu.
Chapter 2 – Field work and methodology

For the analysis of the solvent extract of the natural jarosite clay, an Agilent Technologies 7890A gas chromatograph coupled to a 5975C mass spectrometer was used (Figure 2.33). The gas chromatograph injector was held at 200 °C and operated in splitless mode with a column flow rate of 1.1 mL min\(^{-1}\) and a solvent delay of four and a half minutes. Separation was performed on a J&W DB-5MS UI column (30 m x 0.25 mm x 0.25 µm). The gas chromatograph oven was held for 2 minutes at 40 °C and then ramped to 310 °C at a rate of 5 °C min\(^{-1}\), where it was held for 14 minutes. Mass spectra were acquired in the scan range 40-550 amu.

Figure 2.33. The 7890A gas chromatograph, coupled to a 5975C mass spectrometer was used to analyse the liquid extract from the natural jarosite clay sampled at Brownsea Island.
Chapter 3 - Sulfate minerals: A problem for the detection of organic compounds on Mars?

The work described in this chapter was published in the journal Astrobiology.


Chapter 3 is an adaptation and expansion upon this publication and includes additional figures and details of related unpublished experiments.
Mars global image from NASA/JPL-Caltech (2013)
3.1 Introduction

Organic matter detection missions sent to Mars, the Viking and Phoenix landers and Mars Science Laboratory (MSL) (Map 1), have so far only detected simple chlorinated hydrocarbons that could be either indigenous or exogenous organic matter or contamination from analytical or cleaning procedures prior to launch (Glavin et al., 2013; Leshin et al., 2013). The failure to conclusively detect organic matter in situ is surprising when it is considered that comets, meteorites and interplanetary dust particles have been contributing organic compounds to the red planet throughout its history (Atreya et al., 2007). In addition, organic carbon phases have been detected in martian meteorites (e.g. Sephton et al., 2002; Steele et al., 2012) (Table 3.1) and martian volcanoes, life and serpentinisation could also have produced organic compounds in the past and may still do so today (Atreya et al., 2007). Organic matter is therefore either accumulating at levels below detection limits, is being destroyed by Martian processes (Benner et al., 2000; ten Kate et al., 2005), or its presence is obscured through mission sample processing and analytical procedures.

Table 3.1. Form & carbon isotopes of organic matter in martian meteorites
(Mahaffy et al., 2012)

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Organic matter type</th>
<th>δC(^{13}) (‰)</th>
<th>Lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALH84001</td>
<td>PAHs*</td>
<td>NM</td>
<td>Within carbonates and along silicate grain boundaries</td>
</tr>
<tr>
<td></td>
<td>Macromolecular</td>
<td>~-11</td>
<td>As above</td>
</tr>
<tr>
<td></td>
<td>Carbon</td>
<td>-15</td>
<td>Bulk matrix</td>
</tr>
<tr>
<td>Nakhla</td>
<td>Simple aromatics</td>
<td>~-22</td>
<td>Cracks and grain boundaries</td>
</tr>
<tr>
<td></td>
<td>Macromolecular carbon</td>
<td>~-33 and -15</td>
<td>Unknown</td>
</tr>
<tr>
<td></td>
<td>Macromolecular carbon</td>
<td>~-20</td>
<td>Silicates (i.e. pyroxene/olivine)</td>
</tr>
<tr>
<td>Los Angeles, QUE94201, Shergotty, Zagami, DaG 476, Dho 019, NWA1183, SaU 005, ALH 77005, LEW88516, Y793605,Chassigny.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Data from (Wright et al. 1992; McKay et al. 1996; Grady et al. 1997, 2004; Jull et al. 1998a, 1998b; Becker et al. 1999; Sephton et al. 2002; Steele et al. 2007). *PAHs: Polycyclic aromatic hydrocarbons
Chapter 3 – Sulfate minerals: A problem for the detection of organic compounds on Mars?

Thermal extraction is a technique commonly employed on Mars landers and rovers searching for organic compounds (Biemann et al., 1977; Guinn et al., 2008; Mahaffy, 2008). However, minerals are known to influence the composition of thermal extracts and produce analytical artefacts (Sáiz-Jiménez, 1994; Faure et al., 2006). For example, any mineral species that decomposes to give oxygen on heating may oxidise organic matter present in the sample of interest and render it undetectable. A mineral class that has received a great deal of recent attention is the perchlorates, which are salts containing chlorine and oxygen that thermally decompose to give molecular oxygen on heating (Devlin & Herley, 1986). The Phoenix Lander made the first detection of perchlorates in northern martian soils using the Microscopy, Electrochemistry, and Conductivity Analyzer (MECA) instrument (Chevrier et al., 2009; Hecht et al., 2009; Kounaves et al., 2010; Kounaves et al., 2014). Perchlorate species predominantly decompose at ≤600 °C (Shimokawabe et al., 1977), so their presence on Mars was further implied by Phoenix Thermal Evolved Gas Analyzer (TEGA) results, which showed the evolution of oxygen in the 300 °C - 600 °C range (Hecht et al., 2009). A corresponding release of carbon dioxide detected between 200 °C - 600 °C was tentatively interpreted as resulting from the combustion of organic matter facilitated by perchlorate-sourced oxygen, though no intact organic matter was detected by TEGA (Ming et al., 2009). Similar processes have recently been suggested for historical Viking pyrolysis data (Navarro-González et al., 2010). Perchlorates may form on Mars by gas phase oxidation and are probably widespread in the arid Martian soils (Catling et al., 2010). The Martian meteorite EETA 79001 was found to contain 0.6 ± 0.1 ppm perchlorate (Kounaves et al., 2014). In addition, perchlorate brines may be stable for brief periods of time at the Phoenix landing site (Chevrier et al., 2009). Perchlorates are a potential cause of the detection of chlorinated hydrocarbons and oxygen by the Sample Analysis at Mars (SAM) instrument on MSL (Glavin et al., 2013). A relatively
neglected class of mineral that can decompose to produce atomic oxygen during heating is the sulfates (Holt & Engelkemeir, 1970). The sulfate ion decomposes to sulfur trioxide and then, at higher temperatures, sulfur dioxide and atomic oxygen (Bailey & Smith, 1972). Sulfur trioxide can also combine with water to form sulfuric acid (Wong et al., 2003). The presence of sulfates in mixtures introduced to pyrolysis chambers could therefore pose a similar problem to that observed for perchlorates. If the sulfate is hydrated then the potential generation of sulfuric acid is an additional complication. Thermogravimetric studies show that most sulfates decompose at temperatures greater than 600 °C however iron and aluminium sulfates begin to decompose at temperatures similar to those used for the analysis of macromolecular organic material in pyrolysis studies (Table 3.2) (Mu & Perlmutter, 1981; Sephton & Gilmour, 2001; Sephton et al., 2004; Navarro-González et al., 2006; Sephton, 2012; Sephton et al., 2013).

Table 3.2. Temperature at which the sulfate ion begins to decompose to give sulfur dioxide during thermal decomposition of different sulfate species.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Onset of $SO_4^{2-}$ decomp. (°C)</th>
<th>Decomp. Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jarosite</td>
<td>KFe$_3$(OH)$_6$(SO$_4$)$_2$</td>
<td>501</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Natrojarosite</td>
<td>NaFe$_3$(OH)$_6$(SO$_4$)$_2$</td>
<td>555</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Hydronium jarosite</td>
<td>H$_2$OFe$_3$(OH)$_6$(SO$_4$)$_2$</td>
<td>557</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Ammonium jarosite</td>
<td>NH$_4$Fe$_3$(OH)$_6$(SO$_4$)$_2$</td>
<td>510</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Plumbojarosite</td>
<td>Pb$_{0.5}$Fe$_3$(OH)$_6$(SO$_4$)$_2$</td>
<td>531</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Argentojarosite</td>
<td>AgFe$_3$(OH)$_6$(SO$_4$)$_2$</td>
<td>548</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Alunite</td>
<td>KAl$_3$(OH)$_6$(SO$_4$)$_2$</td>
<td>610</td>
<td>Air</td>
</tr>
<tr>
<td>Natroalunite</td>
<td>NaAl$_3$(OH)$_6$(SO$_4$)$_2$</td>
<td>590</td>
<td>Air</td>
</tr>
<tr>
<td>Hydronium alunite</td>
<td>H$_3$OAl$_3$(OH)$_6$(SO$_4$)$_2$</td>
<td>680</td>
<td>Air</td>
</tr>
<tr>
<td>Ammonium alunite</td>
<td>NH$_4$Al$_3$(OH)$_6$(SO$_4$)$_2$</td>
<td>660</td>
<td>Air</td>
</tr>
<tr>
<td>Ferric sulfate</td>
<td>Fe$_2$(SO$_4$)$_3$</td>
<td>494</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Aluminium sulfate</td>
<td>Al$_2$(SO$_4$)$_3$</td>
<td>580</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Lead sulfate</td>
<td>PbSO$_4$</td>
<td>759</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Magnesium sulfate</td>
<td>MgSO$_4$</td>
<td>780</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>Na$_2$SO$_4$</td>
<td>1100</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Calcium sulfate</td>
<td>CaSO$_4$</td>
<td>1200</td>
<td>Nitrogen</td>
</tr>
</tbody>
</table>

(1) (Frost et al., 2005a) (2) (Frost et al., 2006a) (3) (Frost et al., 2006b) (4) (Frost et al., 2005b) (5) (Rudolph et al., 2003) (6) (Mu & Perlmutter, 1981) (7) (Samadhi et al., 2001) (8) (West & Sutton, 1953).
Jarosite minerals are members of the alunite supergroup (minerals with the general formula $\text{AB}_3(\text{TO}_4)_2(\text{OH})_6$). In jarosite the general formula is characterised by having $\text{Fe}^{3+}$ in the B site and sulfur occupying the T site (Figure 3.1) (Basciano & Peterson, 2008). On Earth a natural solid solution exists in the A site of potassium, sodium and hydronium ions (Brophy & Sheridan, 1965). The A site can also be occupied by ions such as ammonium, lead or silver (Drouet & Navrotsky, 2003). It is well known that variation of the cation species in the A and B sites influences the decomposition temperature of the jarosite structure and that other sulfate species also have highly variable decomposition temperatures (Table 3.2).

Hydronium jarosite will fully decompose from 619 °C when ferric sulfate, an intermediate in its decomposition, breaks down to give iron oxide and sulfur dioxide (sulfuric acid is also produced as a decomposition intermediate and breaks down to give sulfur dioxide at 557 °C (Table 3.2)) (Frost et al., 2006a). With other forms of jarosite the iron in the B site of the general formula will still form a ferric sulfate intermediate, which decomposes at temperatures that are problematic for organic molecule detection, but the A site cation will form a more stable sulfate intermediate, which does not decompose until higher
temperatures (Frost et al., 2005a). Additional metal oxides form during jarosite decomposition, unrelated to the breakdown of sulfate intermediates but the oxygen utilised in their formation is sourced from the hydroxyl groups within jarosite so metal oxides do not act as a sink for oxygen released during the breakdown of the sulfate ions within jarosite (Frost et al., 2005a).

Jarosite is a common secondary mineral in acidic, sulfur-rich environments (Baron & Palmer, 1996). Sulfates, including jarosite, are common on Mars and are interpreted as evidence of surface and near-surface waters present at the time of their formation (Ehlmann et al., 2009). Jarosite can form by the aqueous oxidation of pyrite deposits in a saline, low pH, low water to rock ratio environment (Zolotov & Shock, 2005). Such an environment is thought to have existed in the late Noachian and Hesperian when outgassing from volcanoes released abundant sulfur and water into the Martian atmosphere (Bibring et al., 2006). Noachian and Hesperian terrains are well preserved and widespread on Mars (Michalski et al., 2013). Jarosite is preserved for geological timescales only in extremely arid conditions and the persistence of jarosite on Mars is testament to the planet’s extreme surface aridity in post-Hesperian times (Elwood-Madden et al., 2004).

Sulfur is not just restricted to ancient terrains; the well-mixed dust that covers most surfaces on Mars has a high concentration of sulfur, at an average concentration equivalent to 5.82 wt% SO₃ (Gellert et al., 2004). Magnesium sulfate is a common cementing agent in the upper few centimetres of Martian soil, making up approximately 10 wt% (Vaniman et al., 2004). In situ analyses by landers and rovers support the assertion of widespread sulfates on Mars. Sulfur was detected in Martian soils by the Viking landers at concentrations of 8-15%, with magnesium and sodium sulfates being inferred as the most common mineral phases present.
Chapter 3 – Sulfate minerals: A problem for the detection of organic compounds on Mars?

(Clark & Van Hart, 1981). At the Pathfinder landing site (Map 1) the rover Sojourner’s Alpha-Proton-X-ray-Spectrometer (APXS) found soils to contain a mean value of 6.79% sulfur (Wänke et al., 2001). Opportunity identified the ferric sulfate species jarosite and possibly gypsum at its Meridiani Planum landing site (Map 1; Map 2) (Klingelhofer et al., 2004), and jarosite was present in rocks of the Burns Formation at an abundance of 29% of iron species, the other species being haematite, olivine, pyroxene and magnetite (Morris et al., 2006). Whilst studying Gusev Crater Spirit became embedded in sand in which ferric sulfates were a major phase (Map 1; Map 3) (Arvidson et al., 2010). Sulfur dioxide peaks seen in MSL SAM results from the Rocknest site in Gale Crater (Map 3) were variable but evolved in the form of two main peaks between 450 °C and 800 °C, and were described as consistent with the decomposition of iron sulfates (Leshin et al., 2013). However, analyses at both Rocknest and the Yellowknife Bay study site by the Chemistry & Mineralogy (CheMin) instrument of MSL found only calcium sulfates, suggesting that if iron sulfate is present in the Sheepbed member it exists at levels below detection limits at these locations (Bish et al., 2013; Vaniman et al., 2014). Oxidised sulfur species are widespread in martian meteorites with calcium and magnesium sulfates being the most common forms (Burgess et al., 1989; Gooding, 1992). Mars analogue sites on Earth, such as Río Tinto and Panoche Valley, are notably sulfate rich (Navarro-González et al., 2006).

In this chapter the thermal decomposition of sulfate minerals that are known to exist on Mars and any resulting influence on organic matter detection by thermal extraction methods is assessed. The widespread and abundant nature of sulfates on Mars suggests that any effects will be almost unavoidable for in situ analyses. The behaviour of a natural jarosite clay sample is compared with standards of other common Mars-relevant mineral phases. The data provide
guidance for both interpreting existing data from Mars but also for directing the future operation of thermal extraction units by suggesting routes to mitigate any negative effects of sulfate decomposition on organic detection.

3.2 Materials

Natural samples were collected from the jarosite-coated Parkstone Clay member present on the cliffs running along the southern coast of Brownsea Island, as described fully in Chapter 2. Clay with a thin veneer of jarosite was sampled from the west of the southern coast and much thicker jarosite deposits were sampled from the cliffs at the centre of the coastline (Figure 3.2).

![Figure 3.2. Hand specimens collected from Brownsea Island. Clay with a thin veneer of jarosite can be seen on the left while on the right jarosite rich clay interlayered with iron oxide can be seen in hand specimens collected from the centre of the southern coastline.](image)

Mineral standards were used to aid the interpretation of results from the natural samples. Laboratory standards of ferric sulfate hydrate, calcium carbonate, goethite and quartz were sourced from Sigma Aldrich. Quartz also acted as the procedural blank. Gypsum was acquired from BDH reagents and chemicals. Siderite was synthesised in the laboratory. Illite (IMt-1), kaolinite (KGa-1b) and montmorillonite (Swy-2) were obtained from The Clay Minerals Society. As these are pure single phase standards they are not directly Mars relevant but studying their decomposition augments the analysis of the natural jarosite clay
decomposition and aids interpretation of the relative behaviour of different sulfate species on Mars.

3.3 Characterisation of the natural samples

The natural jarosite samples were analysed using X-ray diffraction (XRD), elemental analysis isotope ratio mass spectrometry (EA-IRMS) and solvent extraction, methods described fully in Chapter 2. The results are discussed in the following sections.

3.3.1 X-ray diffraction

Subsets of the jarosite samples were sent for XRD analysis at the Natural History Museum. The thick jarosite outcrop was found to contain potassium-hydronium jarosite, the thin jarosite outcrop sample also matched this pattern but also matched with pure hydronium jarosite and a reference pattern with the formula Fe$_2$(SO$_4$)$_2$(OH)$_6$, named as carphosiderite. As the pattern for the thick jarosite outcrop was much clearer and there was clearly more jarosite in the sample this was selected for further quantitative analyses and the main experimental work.

3.3.1.1 Quantification of jarosite phases

The thick jarosite outcrop from Brownsea Island was reanalysed quantitatively by XRD and Rietveld refinement. Jarosite was found to make up 5% of the sample in a form between the potassium and hydronium endmembers. Other phases present in the sample were 40% quartz, 36% goethite, 10% Kaolinite and 9% illite.
3.3.1.2 Carphosiderite

The detection of a phase known as carphosiderite in the thin veneer jarosite sample was investigated in case it represented another form of jarosite that might be useful for analysis. The formula given by the International Centre for Diffraction Data (ICDD) database for carphosiderite was confusing as it was listed as $\text{Fe}_2(\text{SO}_4)_2(\text{OH})_5(\text{H}_2\text{O})$. As the hydroxyl groups have a combined charge of minus five and the sulfate ions minus four it is not possible for two iron atoms to balance this charge. The reference pattern for carphosiderite was marked as deleted when the pattern metadata was opened but still matched as a possible phase. If the validity of the formula had not been checked this error may have not been noticed.

It is clear that the phase detected in the thin veneer jarosite sample was not carphosiderite but it remained of interest to discover what the phase actually was. A literature review discovered the term carphosiderite was introduced in 1827 by August Breithaupt using a sample originating from an unknown locality within Greenland, (Breithaupt, 1827). Moss (1957) reassessed Breithaupt’s work and that of other 19th century authors describing carphosiderite and found that the classification methods were erroneous and the samples used were in almost all cases actually sodium jarosite. From the findings of Moss (1957) it would appear that carphosiderite was a redundant term assigned to already classified minerals. However, many authors and glossaries still refer to carphosiderite today and the confusion over what formula it represents persists (Table 3.3). In most cases the term appears when the authors have used XRD to analyse samples. The Powder Diffraction File (PDF) databases published by the ICDD are widely used to pattern match and analyse XRD patterns. There are three files labelled as carphosiderite that exist in both databases. All of these carphosiderite files are marked as deleted by the ICDD. However, the database is structured
so that deleted files are retained, presumably so that the progression to the highest quality reference spectra through time can be followed. A negative effect of this system is that deleted spectra can still be offered as pattern matches for samples analysed by XRD. If a sample is made up of a large number of minerals or there are many samples to run, it is certainly possible that an analyst could use a reference file without consulting the metadata to check its validity.

Moss (1957) concluded that carphosiderite is one of a number of mineral names, “invented by mineralogists only too eager to discover new minerals, and have, in fact, been introduced into the literature by false pretences, in so far as their compositions have been misrepresented, through errors or oversights in the analyses.” However, carphosiderite is still in use today, its existence prolonged primarily due to its presence in the pdf-2 and pdf-4 databases. As the majority of samples used in this PhD contain phases of jarosite it highlights the importance of conducting XRD analyses rather than sending samples to be analysed in other laboratories. Any results sent back that include carphosiderite would be confusing and misleading. When reassessed the thin jarosite outcrop matched well with sodium jarosite patterns. The jarosite in the thin jarosite outcrop therefore appears to be a solid solution of potassium-hydronium and sodium jarosite. To focus the study it was decided for this section

Table 3.3. Present day uses of the term carphosiderite

<table>
<thead>
<tr>
<th>Authors</th>
<th>Description/formula given for carphosiderite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shatalov et al. (2007)</td>
<td>$3\text{Fe}_2\text{O}_3.4\text{SO}_3.5\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Giaveno &amp; Donati (2001)</td>
<td>$\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6.2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Castro et al. (2012)</td>
<td>$\text{Fe}_2(\text{SO}_4)_2(\text{OH})_5(\text{H}_2\text{O})$</td>
</tr>
<tr>
<td>Bachmann et al. (2001)</td>
<td>Named as karphosiderite, no formula given.</td>
</tr>
<tr>
<td>Fernandez-Remolar et al. (2011)</td>
<td>Named as carphosiderite with no formula, authors state they used XRD data.</td>
</tr>
</tbody>
</table>
of work just to study the thick potassium-hydronium jarosite outcrop but the observation of
cation diversity in jarosite in a small study area was indicative that sampling could produce a
range of different jarosite types. The thick jarosite outcrop is hereafter referred to as the
natural jarosite clay sample. The fact that carphosiderite is still appearing in many present
day published works encouraged a collaboration study with the Natural History Museum. In
the synthesis of jarosite described in Chapter 4 the synthesis time was extended to increase
crystal size and allow a new XRD study of a single crystal of sodium jarosite to better
understand the crystal structure.

3.3.2 Determining carbonate versus organic carbon in the natural sample

As carbon dioxide produced during heating would be a potential indicator of the oxidation of
organic matter it was important to check for the presence of carbonates in the natural jarosite
clay, which would also release carbon dioxide. XRD did not detect carbonate in the natural
jarosite clay but this would not rule out trace amounts being present. A subset of the natural
jarosite clay was acid washed to remove carbonate, as described fully in Chapter 2. Samples
of untreated and acid-treated natural jarosite clay were then sent to Iso-Analytical Limited
for EA-IRMS analysis. Both the untreated and acid-treated natural jarosite clay were found to
have a carbon content of 0.45% by EA-IRMS indicating that there is no significant carbonate
component in the sample and that the carbon observed is organic carbon. Subsamples of equal mass of the untreated and acid-washed natural jarosite clay were
pyrolysed at 1000 °C. The two chromatograms were extremely similar, there was a very small
decrease in the peak heights for carbon dioxide and sulfur dioxide in the acid washed sample.
The reduction in peak height suggests that acid washing dissolved a small amount of the
jarosite and organic matter present in the natural jarosite clay (Figure 3.3).
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Figure 3.3. The production of light gases during pyrolysis of untreated and acid washed natural jarosite clay. The m/z 28 peak is labelled as CO? as it could be either carbon monoxide or nitrogen; carbon monoxide is inferred as discussed in the text.
3.3.3 Solvent extraction

Solvent extraction using 95:5 dichloromethane-methanol indicated that the carbon phases in the natural jarosite clay include extractable organic matter indicative of higher plant matter (alkanes, methyl tetradecanoate, hexanol, and carboxylic acids) (Figure 3.4) (Table 3.4). The natural jarosite clay was also contaminated by the plasticizer n-butyl-benzenesulfonamide. Contamination likely occurred during sample collection as the samples were very wet due to rain on the day of field work and were stored in plastic bags during transport.

![Figure 3.4. The chromatogram produced from gas chromatography-mass spectrometry (GC-MS) analysis of the solvent extract of the natural jarosite clay. ?: Peaks that could not be identified with confidence; A: These peaks are alkane chains but the exact chain length could not be resolved.](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-hexanol, 2-ethyl</td>
<td>6</td>
<td>Hexadecanoic acid, methyl ester</td>
<td>11</td>
<td>Hexadecane</td>
</tr>
<tr>
<td>2</td>
<td>Undecane</td>
<td>7</td>
<td>n-hexadecanoic acid</td>
<td>12</td>
<td>Heptadecane</td>
</tr>
<tr>
<td>3</td>
<td>Butylated hydroxytoluene</td>
<td>8</td>
<td>9-octadecenoic acid, methyl ester</td>
<td>13</td>
<td>Nonadecane, 9 methyl</td>
</tr>
<tr>
<td>4</td>
<td>Methyl tetradecanoate</td>
<td>9</td>
<td>Octadecanoic acid, methyl ester</td>
<td>14</td>
<td>Octadecane</td>
</tr>
<tr>
<td>5</td>
<td>Benzenesulfonamide, N-butyl-</td>
<td>10</td>
<td>1,2-benzenedicarboxylic acid, mono(2-ethylhexyl) ester</td>
<td>15</td>
<td>Eicosane</td>
</tr>
</tbody>
</table>

Table 3.4. Species identified in the solvent extract of the natural jarosite clay
3.4 Experimental parameters

The experiments described in this thesis focus mostly on natural samples rather than laboratory standards for several reasons. Firstly, jarosite analysed in situ on Mars will likely be present as a small percentage of a well-mixed sample (Morris et al., 2006). Secondly the jarosite structure can undergo multiple substitutions (Basciano & Peterson, 2008), and as cations exert a significant influence on decomposition temperature (Table 3.2) a natural jarosite clay was chosen so that the decomposition was representative of a natural cation ratio rather than a synthetic sample, which may be unnaturally enriched in a particular cation.

In the project described in this chapter the natural jarosite clay from Brownsea Island was investigated and supporting data provided by laboratory standards. Powdered samples were placed into quartz pyrolysis tubes and held in place by quartz wool. With all samples, other than siderite, 4 mg of sample was used; the siderite experiment used only 3 mg, because the response of carbon dioxide is much greater for siderite relative to the other minerals. For the natural jarosite clay (Figure 3.5) and ferric sulfate hydrate experiments multiple individual samples (i.e. samples run at one temperature step only, rather than using stepped pyrolysis) were run at 100 °C intervals, the lowest at 400 °C and the highest at 1000 °C, allowing both the products of pyrolysis and the variation in decomposition rate at different temperatures to be investigated. An additional individual analysis at 550 °C was used to focus on decomposition around typical pyrolysis temperatures used for studying macromolecular organic material (Mu & Perlmutter, 1981; Sephton & Gilmour, 2001; Sephton et al., 2004; Navarro-González et al., 2006; Sephton, 2012; Sephton et al., 2013). For each of the other minerals being studied two individual experiments were carried out, one at 600 °C and one at 1000 °C to show the decomposition at typical pyrolysis temperatures and at the higher
temperature to identify any species released under the full range of typical pyrolysis conditions. Additional individual natural jarosite clay samples were pyrolysed at 600 °C and 700 °C with the gas chromatograph and mass spectrometer (GC-MS) optimised for organic molecule detection (Figure 3.7).

Stepped pyrolysis experiments, those most similar to the heating experiments being carried out by Curiosity, are carried out in Chapter 4. The work in this chapter was designed to test if sulfate minerals exerted any influence on the detection of organic compounds through pyrolysis. Heating a sample at one temperature step only ensures that all materials that will break down up to the set temperature do so at the same time and consequently the chance of observing secondary reactions between the products of pyrolysis is maximised.

Figure 3.5. The powdered natural jarosite clay from Brownsea Island. The earthy orange colour is due to the goethite that makes up a significant proportion of the sample.
3.5 Thermal decomposition of ferric sulfates

The major gases released by the natural jarosite clay at 600 °C and 1000 °C were carbon dioxide, water and sulfur dioxide (Figure 3.6). A minor peak of mass to charge ratio (m/z) 28 was also detected at both temperatures, which could be either nitrogen or carbon monoxide as both species have the same mass and retention time. It is inferred that this species is carbon monoxide as it is an expected product of partial combustion, the peak area increased with temperature and no m/z 28 peak was seen in any other sample apart from siderite.

![Figure 3.6. Total ion current chromatograms of the gaseous products released during individual heating experiments of samples of a natural jarosite clay and a lab standard of ferric sulfate hydrate at 600 °C and 1000 °C. The m/z 28 peak is labelled as CO? as it could be either carbon monoxide or nitrogen; carbon monoxide is inferred as discussed in the text. Very minor peaks for oxygen and carbon dioxide were present in the ferric sulfate hydrate experiment at 600 °C but cannot be seen at the scale of the figure. All chromatograms are presented at the same scale.](image-url)
(Figures 3.7 & 3.8). Oxygen was not detected at either temperature step for the natural jarosite clay.

The lack of carbonate phases in the XRD data for the natural jarosite clay, along with identical EA-IRMS total carbon values for the untreated and acid-treated samples, indicate that the carbon dioxide detected was derived from the breakdown of organic matter and not carbonate decomposition. Pyrolysis data for untreated and acid-treated natural jarosite clay samples are almost identical confirming the absence of significant carbonate because pyrolysis of a carbonate-containing sample would have generated much less carbon dioxide after being treated with acid.

The substantial peaks for sulfur dioxide indicate decomposition of the sulfate ions within jarosite and therefore decomposition to sulfur trioxide and then sulfur dioxide and oxygen (Bailey & Smith, 1972). However, as neither sulfur trioxide nor oxygen were detected directly it is inferred that sulfur trioxide broke down rapidly and oxygen was completely consumed in the oxidation of organic matter. The oxidation of organic matter is therefore responsible for the majority of the carbon dioxide detected. Pyrolysis-GC-MS of the natural jarosite clay, scanning in the range 45-550 atomic mass units (amu) with a DB-5MS UI column, found only sulfur dioxide was detectable in the pyrolysis products with a very minor benzene peak at 700 °C (Figure. 3.7). None of the organic compounds isolated through solvent extraction were detected by pyrolysis-GC-MS. At pyrolysis temperatures these compounds were converted to carbon dioxide. These observations suggest that jarosite decomposition can act as an oxidiser of organic matter.
At 600 °C the lab standard of ferric sulfate hydrate produced distinct peaks for water and sulfur dioxide and extremely minor peaks for carbon dioxide and oxygen (Figure 3.6). The sulfur dioxide peak area was substantially greater at 1000 °C and was accompanied by an oxygen peak. Carbon dioxide was present at low levels during both the 600 °C and 1000 °C temperature steps. Only in the 1000 °C experiment was the response great enough to be clearly visible in the chromatogram (Figure 3.6). The carbon dioxide data suggested the thermal decomposition of a mineral impurity or minor contamination by organic compounds in the lab standard. Decomposition of sulfate ions can produce detectable oxygen during pyrolysis GC-MS. Sulfur trioxide was not detected suggesting it breaks down rapidly to sulfur dioxide and oxygen at temperatures equal or greater than 600 °C.

3.6 Thermal decomposition of laboratory standards

The clay minerals and goethite present in the natural jarosite clay could be responsible for a major proportion of the water evolved during heating, which can be tested by the study of laboratory standards (Figure 3.8). For the goethite standard, oxygen was present at low levels
during both the 600 °C and 1000 °C experiments. However, only at 1000 °C was the response clearly visible at the scale of the chromatogram.

To investigate if goethite could have contributed significant oxygen during decomposition of the natural jarosite clay, pyrolysis of the goethite standard was repeated using individual experiments at 100 °C increments between 600 °C and 1000 °C. When plotted on the same axes as the natural jarosite clay data, oxygen released by the goethite standard plots as a flat
line and can be ruled out as a significant contributor of oxygen in the natural jarosite clay heating experiment. A minor carbon dioxide peak was seen at both temperatures for goethite, which suggests the presence of minor organic contamination in the lab standard. A distinct carbon dioxide peak was seen at 1000 °C for illite but none was detected at 600 °C. The data suggest decomposition of a carbonate impurity as organic matter would have suffered substantial decomposition at 600 °C. Quartz was inert at both temperatures and indicated that the experimental procedure did not contaminate the samples. Overall, none of the minerals analysed can be implicated in the natural jarosite clay low temperature carbon dioxide peak so combustion of organic matter remains the most probable source.

Variation in clay species does not appear to be an issue. Montmorillonite released water at both 600 °C and 1000 °C and carbon dioxide appeared during the 1000 °C step (Figure 3.9). The carbon dioxide was again related to a carbonate impurity; a source by organic matter contamination is unlikely because of a lack of carbon dioxide detection at 600 °C. Siderite decomposes at both 600 °C and 1000 °C to give carbon dioxide and a m/z 28 peak. The m/z 28 peak is interpreted as carbon monoxide rather than nitrogen due to the homogeneity of the sample and the decomposition products of siderite being well known (Gallagher & Warne, 1981). Although siderite is a potential source of carbon dioxide, the XRD and EA-IRMS analyses show carbonate is absent in the natural jarosite clay so siderite is not a plausible source of significant carbon dioxide in this sample. Gypsum was pyrolysed and as expected from previous work (West & Sutton, 1953), it only dehydrated, suggesting that this common sulfate is relatively stable at pyrolysis temperatures used for the detection of organic matter. In summary, the data from these experiments studying the decomposition of other relevant mineral phases suggest that carbon dioxide released from the natural jarosite clay must
primarily originate from oxidation of organic matter by oxygen derived from jarosite decomposition.

Figure 3.9. Total ion current chromatograms of the gaseous products during individual heating experiments of lab standards representing other Mars-relevant minerals at 600 °C and 1000 °C. All chromatograms are presented at the same scale.
3.7 Thermal decomposition of ferric sulfates between 400 °C – 1000 °C

With the sources of the pyrolysis products from the decomposition of relevant mineral phases assessed, further work was performed to examine the relative response of pyrolysis products for the ferric sulfates with temperature (Figure 3.10). The peak areas were normalised to the abundance of sulfate in the sample (100% for the ferric sulfate hydrate and 5% of sample mass for the natural jarosite clay).

Figure 3.10. The production of sulfur dioxide, carbon dioxide, possible carbon monoxide and oxygen during the thermal decomposition of samples of natural jarosite clay and a lab standard of ferric sulfate hydrate in individual heating experiments carried out between 400 °C and 1000 °C at 100 °C increments. *The peak areas were normalised by sulfate mass (100% in ferric sulfate hydrate, 5% of sample mass in the natural jarosite clay – from XRD results). The m/z 28 peak is labelled as CO? as it could be either carbon monoxide or nitrogen, carbon monoxide is inferred as discussed in the text.
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The natural jarosite clay sample and synthetic ferric sulfate hydrate both began to decompose to produce sulfur dioxide at temperatures which approximate those used for the flash pyrolysis of macromolecular organic matter (around 600 °C). Yet, the peak area for sulfur dioxide produced from jarosite decomposition was much greater than that seen in ferric sulfate. Sulfur dioxide contributions from other minerals in the sample are implausible sources because XRD indicated that there are no other sulfates present in the natural jarosite clay.

Oxygen was not detected during heating of the natural jarosite clay but was detectable in the ferric sulfate hydrate experiments at temperatures at and above 600 °C (Figure 3.10). A substantial response for carbon dioxide appears at low temperatures for the natural jarosite clay from 500 °C and a more limited response is evident at high temperatures from the ferric sulfate hydrate. The peak area of the m/z 28 compound increases up to 550 °C and its response is relatively constant thereafter in the natural jarosite clay. The rapid increase of carbon dioxide at temperatures normally associated with the decomposition of organic matter suggest the combustion of organic matter aided by sulfate-sourced oxygen. The peak areas for sulfur dioxide, water and the m/z 28 compound produced by the natural jarosite clay are very similar at 800 °C and higher indicating that the hydronium and ferric sulfate components in the potassium-hydronium jarosite were breaking down rapidly. The ferric sulfate hydrate peak areas were still increasing at 1000 °C indicating that full decomposition in the synthetic sample had not yet been achieved. Oxygen increased with sulfur dioxide in the ferric sulfate hydrate experiments. Jarosite appears to break down rapidly at temperatures commonly used in thermal decomposition studies of organic matter.
To better understand the production of sulfur dioxide and carbon dioxide during pyrolysis of the natural jarosite clay the peaks areas were quantified with reference to calibration curves (Table 3.5). Sulfur dioxide was calibrated by manual injections of known volumes of gas and carbon dioxide through the pyrolysis of different masses of sodium bicarbonate. If the entire carbon content (0.45%) of the natural jarosite clay was oxidised then 1 mg would be expected to produce 0.0165 mg of carbon dioxide. The greatest mass of carbon dioxide produced per mg of the natural jarosite clay was 0.0112 mg at 600 °C indicating that 68% of the carbon in the sample had been lost as carbon dioxide. Approximately a third of the organic carbon present must therefore be refractory and inaccessible by pyrolysis or combustion at temperatures ≤1000 °C.

### Table 3.5. Carbon dioxide, sulfur dioxide, and theoretical oxygen production per mg of sample during individual pyrolysis runs of the natural jarosite clay.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Mass SO₂ (mg)</th>
<th>Theoretical mass of O₂ release during sulfate decomposition* (mg)</th>
<th>Mass CO₂ (mg)</th>
<th>C/O₂ molar ratio**</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0</td>
<td>0</td>
<td>0.0021</td>
<td>-</td>
</tr>
<tr>
<td>500</td>
<td>0.0020</td>
<td>0.0010</td>
<td>0.0057</td>
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</tr>
<tr>
<td>550</td>
<td>0.0104</td>
<td>0.0052</td>
<td>0.0099</td>
<td>1.37</td>
</tr>
<tr>
<td>600</td>
<td>0.0155</td>
<td>0.0078</td>
<td>0.0112</td>
<td>1.05</td>
</tr>
<tr>
<td>700</td>
<td>0.0190</td>
<td>0.0095</td>
<td>0.0110</td>
<td>0.84</td>
</tr>
<tr>
<td>800</td>
<td>0.0224</td>
<td>0.0112</td>
<td>0.0089</td>
<td>0.58</td>
</tr>
<tr>
<td>900</td>
<td>0.0228</td>
<td>0.0114</td>
<td>0.0085</td>
<td>0.54</td>
</tr>
<tr>
<td>1000</td>
<td>0.0217</td>
<td>0.0109</td>
<td>0.0087</td>
<td>0.58</td>
</tr>
</tbody>
</table>

*During sulfate decomposition SO₂ release is double O₂ (Holt & Engelkemeir, 1970)
** Moles of carbon in CO₂ divided by the moles of O₂ released by sulfate decomposition.

All of the oxygen in the carbon dioxide mass produced at ~600 °C and above could be oxygen sourced from sulfate decomposition (Table 3.5). The lower temperature carbon dioxide that is not sourced from oxidation must still originate from the thermal processing of organic carbon because carbonates are not present in the sample. The decarboxylation of carboxylic acids (which were detected in the solvent extract) are likely to be responsible (Alencar et al.,
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1983). Decarboxylation explains the mass of carbon dioxide detected at 400 °C (Table 3.5) which appears before any sulfate decomposition is occurring in the natural jarosite clay. Consequently, the data indicate that oxygen sourced from jarosite decomposition can oxidise a major proportion of indigenous organic carbon in a sample.

3.8 Implications and discussion

It is clearly evident from the data that sulfate minerals represent a potential problem for the detection of organic matter on Mars by thermal extraction methods. Sulfates are abundant in martian rocks, regolith and the well mixed globally spread dust. Here it has been demonstrated that a well-mixed natural jarosite clay containing 5% jarosite can decompose at and above 500 °C to release sulfur dioxide, and therefore oxygen, and in the process oxidise indigenous organic matter. Ferric sulfate hydrate also begins to decompose at similar temperatures to give sulfur dioxide. Gypsum and magnesium sulfate are unlikely to yield oxygen at the temperatures commonly employed for the thermal extraction of organic matter. Much attention has been focused on the potential for perchlorate salts to disrupt thermal extraction experiments; the data highlights that ferric sulfates should also be treated as a potential additional complication. Thermogravimetric studies suggest that aluminium sulfates may also disrupt organic detection experiments (Rudolph et al., 2003).

This sulfate data can be used to re-examine past experiments on Mars. Viking lander thermal volatilisation-gas chromatography-mass spectrometry (TV-GC-MS) data has been reinterpreted to suggest that the decomposition of minerals, specifically perchlorates, may have precluded the detection of organic matter (Navarro-González et al., 2010). This reinterpretation was questioned by Biemann & Bada (2011) who state that Viking data are not consistent with chlorination or oxidation of organic matter by perchlorates. Sulfates have
not yet been directly considered as an additional confounding mineralogy during analysis on Mars. Inorganic chemical investigation onboard the Viking Landers revealed high levels of sulfur (Clark et al., 1977). However, sulfur-containing compounds were absent in data from pyrolysis experiments at temperatures of 500 °C and below (Biemann et al., 1977). Comparison of the sulfate data from this chapter to those from the Viking experiments suggests that no potassium jarosite was present at the sample sites. Ferric sulfate may have been present but pyrolysis temperatures would have been too low for substantial decomposition (Figure 3.10). This comparison suggests that even when confounding mineralogies exist, temperature windows can be identified within which pyrolysis studies can take place, which is investigated further in Chapter 4.

Jarosite was inferred as a possible contributor to a water release detected between 295 °C and 735 °C by TEGA at the Phoenix landing site (Smith et al., 2009). However no sulfur dioxide was detected in the heating range of 25-1000 °C (Golden et al., 2009). The data in this chapter show that jarosite can therefore be removed from the list of potential dehydrating minerals suggested by Smith et al. (2009). Gypsum was interpreted as a possible phase in the Phoenix landing site soil (Hecht et al., 2009). An interpretation consistent with the findings of this project, which shows that gypsum is unlikely to decompose to give sulfur dioxide below 1000 °C.

Recently, pyrolysis of surface materials from the Rocknest aeolian deposit in Gale Crater led to the simultaneous release of oxygen and chlorinated hydrocarbons suggesting the influence of perchlorates on organic decomposition (Glavin et al., 2013). Sulfur dioxide release was variable suggesting heterogeneity in sulfur minerals, but a recognisable bimodal distribution existed with two peaks centred at ~500 to 550 °C and ~700 to 750 °C (Leshin et al., 2013).
Notably the lower temperature release of sulfur dioxide was accompanied by an increase in carbon dioxide. As the lower temperature carbon dioxide peak was significantly larger than sulfur dioxide it is primarily consistent with the thermal decomposition of siderite (Leshin et al., 2013). However, it is possible that perchlorate decomposition-induced oxidation led to the degradation of organic matter at lower temperatures (ca. 350 to 450 °C), while jarosite decomposition-induced oxidation at slightly higher temperature (ca. 450 °C to 550 °C) exhausted any remaining organic matter with the resulting carbon dioxide peak obscured by siderite decomposition (Leshin et al., 2013).

The carbon dioxide and carbon monoxide produced by siderite decomposition could be misinterpreted as evidence of the combustion of organic matter so interpretation of siderite containing samples is extremely challenging. Multiple minerals may be complicating the search for indigenous organic matter on Mars. MSL pyrolysis of mudstone samples at

![Figure 3.11. Gases released during heating of Rocknest samples. Plot A shows the most abundant ions diagnostic of specific gases evolved during pyrolysis, plot B shows minor gases evolved during Rocknest run 4 (Leshin et al., 2013).](image)
Yellowknife Bay also produced chlorinated hydrocarbons and a sulfur dioxide peak centred at 600 °C, however mudstones are indicative of neutral waters, rather than the low pH conditions needed for the formation of iron sulfates, so sulfides are the more realistic sulfur source at this locality (Ming et al., 2014). Though sulfates are widespread on Mars, the types of sulfur species found at each locality seem to be highly variable. The data recently released for pyrolysis at Confidence Hills in jarosite bearing strata are discussed in Chapter 4 as the experimental work discussed in that chapter produced the results closest to that seen at Confidence Hills.

The negative influence of sulfate minerals on organic detection is magnified when it is noted that organic matter and sulfates have been observed to co-locate in terrestrial Mars analogue environments. Sulfates are an indicator of the presence of past liquid water, which is a prerequisite for the creation of habitable environments that can support life and its biochemistry. Glycine has been shown to associate with terrestrial jarosite samples and influence their decomposition (Kotler et al., 2009). It has been demonstrated that organic material can be preserved in ancient terrestrial sulfate minerals (Aubrey et al., 2006). Sulfate rich Mars analogue sites, such as Río Tinto and Panoche Valley, were found to have severely attenuated organic responses in thermal volatilization experiments by Navarro-González et al., (2006) but the decomposition of sulfate ions to give oxygen was not one of the confounding mechanisms considered by the authors. It appears that sulfates on Mars may represent something of a mixed blessing, acting as an effective host for organic matter but also reflecting a potentially aggressive material that is difficult to analyse. The possible co-location of organic matter with sulfate minerals on Mars makes avoiding sulfates an unsatisfactory mitigation step and other options must be considered. Only certain sulfates
Chapter 3 – Sulfate minerals: A problem for the detection of organic compounds on Mars?

decompose to produce sulfur dioxide and then oxygen at the temperatures used for the detection of organic matter. A preliminary mineralogical analysis allows the risk of sulfate interference to be assessed. Such a method is used by MSL where SAM results can be compared with data from the CheMin instrument (Glavin et al., 2013). If jarosite is detected it would be a strong contender for the source of sulfur dioxide, water and potentially oxygen and high temperature carbon dioxide peaks (the latter being derived from the oxidation of organic matter) seen in thermal extraction experiments. In addition, the carbon dioxide peaks resulting from perchlorate and/or sulfate oxidation on Mars can be interpreted to indicate the relative molecular weights of organic compounds being oxidised and potentially differentiate contamination from indigenous organic compounds (Sephton et al., 2014). Contamination is typically made up of mobile low weight organic matter, which would produce a low temperature carbon dioxide peak when oxidised (Sephton et al., 2014). High weight organic matter is typically indigenous and would produce a high temperature carbon dioxide peak when oxidised (Sephton et al., 2014).

3.9 Conclusions

Sulfate minerals are commonly found on Mars. Iron sulfate species such as jarosite and ferric sulfate experience breakdown of their sulfate structures, and therefore release oxygen, at pyrolysis temperatures used to thermally extract organic matter. Sulfate decomposition can lead to the introduction of oxygen and/or sulfuric acid to pyrolysis chambers. Martian ferric sulfates therefore represent a significant complication to organic detection through heat-based methods. A large peak of carbon dioxide and a minor peak representing carbon monoxide were detected during pyrolysis of a natural jarosite clay sample suggesting that the organic content is being combusted by oxygen released by jarosite decomposition. The
prevalence of sulfates in Martian rocks, regolith and the globally mixed dust means that they are difficult to avoid. In addition terrestrial sulfates have been shown to associate with organic compounds so avoiding these minerals on Mars during organic detection experiments would be unwise. Previous authors have recognised that the decomposition of perchlorates on Mars may degrade organic matter. Sulfates may also be contributing to the oxidation of organic matter during thermal analyses, thereby complicating interpretations. However, the relatively high breakdown temperatures for sulfates means that a combination of preliminary mineralogical analyses and suitably selected thermal extraction temperatures may minimise or remove their negative influence.
Chapter 4 – A quantitative study of the oxidising potential of jarosite in thermal experiments on Mars: Assessing the role of cation variation and the use of natural versus synthetic proxies
Mars global image from NASA/JPL-Caltech (2013)
4.1 Introduction

Organic compounds on Mars are likely to be at low concentrations and jarosite is known to occur at many locations, sometimes at high abundance, so the discovery of the mineral’s detrimental influence on organic matter detection (Figure 4.1) (Lewis et al., 2015) has a significant impact on the operation of thermal experiments on Mars (Benner et al., 2000; Klingelhoefer et al., 2004; ten Kate et al., 2005; Milliken et al., 2008; Lewis et al., 2015; Rampe et al., 2015;).

Though the natural jarosite clay was well characterised, and oxygen derived from jarosite decomposition was clearly causing oxidation of organic matter, the release of oxygen from jarosite was not directly observed. The atomic oxygen produced by sulfate decomposition is extremely reactive so its absence in the detectable pyrolysis products of a complex mixture of minerals and organic matter is not surprising (Holt & Engelkemeir, 1970). Pure-synthetic standards would allow the production of oxygen from jarosite to be studied and quantified directly.

Figure 4.1. A clay and iron oxide rich sample from Brownsea Island, which hosts jarosite and organic matter, was found to give a very poor response for organic compounds during pyrolysis-gas chromatography-mass spectrometry (py-GC-MS) (Chapter 3). Jarosite on Mars represents a major complication for experiments searching for trace amounts of organic matter through in-situ heating experiments.
Chapter 4 – A quantitative study of the oxidising potential of jarosite in thermal experiments on Mars

In this chapter the following questions are investigated:

1. How much oxygen does jarosite release during thermal decomposition?
2. How does jarosite behave in stepped pyrolysis experiments?
3. How do different forms of jarosite decompose during stepped pyrolysis?
4. Are synthetic jarosite samples a good proxy for natural samples?
5. During the stepped pyrolysis of natural samples containing different forms of jarosite do the differing sulfur dioxide and carbon dioxide peaks correlate as evidence of high temperature organic matter oxidation?
6. How does the decomposition of jarosite influence the detection of alkanes, alkenes and dienes during thermal extraction-based experiments?

4.1.1 Cation variation in jarosite

The alunite supergroup, of which jarosite is a member, has the general formula \( \text{AB}_3(\text{TO}_4)_{2}(\text{OH})_6 \) (Basciano & Peterson, 2008). The A site can be occupied by monovalent, divalent, trivalent or quadrivalent ions while in the B site aluminium or iron are most common but gallium or vanadium can also be present (Stoffregen et al., 2000). Minerals with Fe>Al belong to the jarosite group while those with Al>Fe are in the alunite group (Dutrizac & Jambor, 2000). The T site can be occupied by sulfur, arsenic or phosphate with both alunite and jarosite being sulfur dominated (Stoffregen et al., 2000). The alunite structure has been unflatteringly referred to as a “garbage can” due to its ability to accommodate many different elements (Swayze et al., 2008).

Despite the diversity of ions that can be incorporated into the alunite structure, most natural jarosite occurrences are sodium or potassium rich with minor hydronium substitution (Dutrizac & Jambor, 2000; Drouet & Navrotsky, 2003). The alkali ions can be sourced from
groundwater or from local aluminosilicates or glauconite leached by the low pH solutions developed by sulfide oxidation (Dutrizac & Jambor, 2000). Alkali sulfates are highly mobile and alkali dominant jarosite can therefore form at considerable distance from the oxidising sulfides that contribute iron and sulfur (Dutrizac & Jambor, 2000). The occasional occurrence of jarosite pseudomorphs after pyrite indicate that at these locations the groundwater must have contained enough potassium or sodium to form jarosite immediately at the site of pyrite oxidation (Dutrizac & Jambor, 2000). Potassium jarosite is the most thermodynamically stable form so only solutions with a high sodium to potassium ratio will give natrojarosite, depletion of both sodium and potassium in fluids leads to hydronium jarosite formation (Dutrizac & Jambor, 2000). Hydronium substitution is more common in jarosite than in alunites formed at similar temperatures as jarosite typically forms in lower pH fluids that have greater hydronium activity (Stoffregen et al., 2000). Pure endmember compositions are rare in both natural and synthetic samples (Stoffregen et al., 2000). However, analyses of natural materials suggest solid solution for potassium and sodium in jarosite may not actually occur and instead samples are discrete mixtures of potassium and sodium endmembers (Swayze et al., 2008). The unit cell dimensions of jarosite vary with substitutions into the trigonal (hexagonal) alunite structure and these variations can be used to estimate potassium, sodium and hydronium abundance (Papike et al., 2006; Basciano & Peterson, 2008; Desborough et al., 2010).

Jarosite typically forms in highly-acidic oxidising environments, such as the weathering zone of pyrite bearing ores (supergene jarosite), in acid saline lakes, sulfate-rich waters from pyrite oxidation or aerosols from seawater (sedimentary jarosite), or in hot springs and epithermal environments where oxidation of hydrogen sulfide is occurring (hydrothermal jarosite)
Chapter 4 – A quantitative study of the oxidising potential of jarosite in thermal experiments on Mars

(Figure 4.2) (Papike et al., 2006). In addition, microbial processes often influence jarosite formation (Desborough et al., 2010). Hydrothermal jarosite is the most stable form and appears to contain little to no hydronium (Swayze et al., 2008).

![Diagram illustrating the formation mechanisms of supergene and hydrothermal jarosite deposits.](image)

Figure 4.2. Diagram illustrating the formation mechanisms of supergene and hydrothermal jarosite deposits. Two oxidation steps for SO₂ are required, firstly an interaction with water that produces H₂S and H₂SO₄ and then oxidation of H₂S to create the low pH conditions that maintain jarosite stability. On Earth atmospheric oxygen oxidises H₂S to H₂SO₄ and Fe²⁺ to Fe³⁺. On Mars atmospheric CO₂ reduction to CO is a possible oxidation mechanism. Oxidation occurs in the vadose zone where rocks are unable to buffer the pH (Papike et al., 2006).

Jarosite eventually alters to goethite when it is removed from its stability field (Dutrizac & Jambor, 2000). A potential pathway for the formation of jarosite on Mars was the release of sulfur gases from shallow magmas which came into contact with water and formed sulfate and hydrogen sulfide, leading to the circulation of low-pH fluids (Papike et al., 2006). The detection of hydronium-bearing jarosite by the Compact Reconnaissance Imaging spectrometer for Mars (CRISM) on board Mars Reconnaissance Orbiter (MRO) suggests jarosite formation in acidic low-temperature environments (Swayze et al., 2008).

The large concentration of potassium in jarosite makes it a useful mineral for age determination by potassium-argon dating (Stoffregen et al., 2000). Using this method hydrothermal jarosite deposits found in Chihuahua, Mexico were found to have an age range of 0.4 to 10 Ma (Papike et al., 2006). Though some hydrothermal deposits appear to be long
lasting on Earth, hydronium jarosite seems to be particularly unstable over geological timescales (Swayze et al., 2008). Currently the observation of jarosite on Mars can be used to identify deposits that were altered by low-pH conditions and alkali-rich brines. Sample return missions (Figure 4.3) would allow radiogenic dating techniques to establish the age of deposition and sulfur, oxygen and hydrogen isotopes would provide information on the temperature of formation, depositional environments and the source of fluids (Papike et al., 2006).

Figure 4.3. A sample return mission would allow Earth based laboratories to unlock the full analytical potential of martian jarosite and provide information about the timing of sulfate formation, as well as fluid temperatures and sources (Mattingly & May, 2011).
### Chapter 4 – A quantitative study of the oxidising potential of jarosite in thermal experiments on Mars

#### 4.2 Characterisation of natural samples

One of the main aims of the work described in this chapter is to better understand the decomposition of different forms of jarosite. With this in mind the natural samples collected from St. Oswald’s Bay in 2012 and the Lake District in 2013 were investigated as they represent a range of formation environments. X-ray diffraction (XRD) and acid washing combined with pyrolysis at 1000 °C were used to characterise the mineral phases and estimate the proportion of organic to inorganic carbon in the samples.

##### 4.2.1 Materials collected at St. Oswald’s Bay

Phase identification using XRD revealed that the jarosite bearing layers found around the acidic stream in 2012 (named as Pequeño Río Tinto (PRT)) matched well with XRD reference patterns for potassium jarosite and quartz. The decomposed pyrite nodule in the Gault and Greensand hosted sodium jarosite (this sample was labelled as GS). The jarosite containing layers found near the stairs from the Durdle Door were a complex mixture of jarosite, clays and iron oxide. It was decided to experiment on the potassium jarosite sample from the acidic stream environment (labelled as PRT) as it was a simple two phase mixture and the lack of iron oxide suggested it was very fresh. Phase quantification of GS using XRD and Rietveld refinement found 25% sodium jarosite, 59% gypsum, 9% quartz and 7% calcite. PRT contained 42% potassium jarosite and 58% quartz. The co-location of jarosite and carbonate in GS is unusual as carbonate is not preserved in acidic jarosite forming environments and it suggests that the acidic conditions created by pyrite oxidation around the nodule were extremely localised. Sampling presumably acquired both the jarosite nodule and carbonate phases from the surrounding Gault and Greensand.
Acid washed samples showed several significant differences during pyrolysis at 1000 °C relative to untreated samples (Figure 4.4). Pyrolysis of an untreated sample of GS produced major peaks for carbon dioxide, sulfur dioxide and water, which are expected from a sample containing carbonate and hydrated sulfates. The acid washed sample of GS sample produced a significantly weaker peak for carbon dioxide, a slightly reduced peak for water, an enhanced peak for sulfur dioxide and peaks for oxygen and benzene that were not present in the untreated sample. The removal of carbonate by the acid washing explains the smaller carbon
dioxide peak. The residual carbon dioxide and the presence of benzene suggests some organic matter is present in GS.

The enhancement of sulfur dioxide in the acid treated sample was unexpected. There are several possible causes but sample heterogeneity and grain size differences were minimised by stirring, crushing and homogenisation in a pestle and mortar prior to the experiments. This issue is explored later in Section 4.6. The detection of oxygen shows that acid washing removed a sink for oxygen derived from jarosite decomposition.

The mass to charge ratio (m/z) 28 peak detected during the pyrolysis of a sample of untreated PRT was inferred to be carbon monoxide rather than nitrogen due to its association with a substantial carbon dioxide peak and absence in the other chromatograms. An acid washed sample of PRT showed a reduction in carbon dioxide production and an absence of carbon monoxide. It is inferred that this was not due to carbonate removal. PRT was forming directly in an acidic stream in which carbonate formation and preservation would be impossible. It is believed that acid washing removed or altered some of the organic matter in the sample. Evidence for this is seen in the detection of acetic acid in the untreated sample and its absence in the acid-washed sample. Sulfur dioxide is unchanged suggesting acid washing does not significantly affect jarosite. Benzene was detected in both untreated and acid-washed PRT but it produced a greater peak in the acid-washed sample. Acid washing appears to enhance the production of benzene in both samples. As with GS, acid washing of PRT removed a sink for oxygen produced by jarosite decomposition. Though it is not possible to quantify amounts with this method, both samples appear to contain some organic matter.
4.2.2 Materials collected in the Lake District

As the materials collected from the Sandbed Mine were from dumped mine wastes compositional variation is likely to be significant. Instead of analysing every hand sample with XRD the crushed and homogenised powders from each specimen were pyrolysed at 1000 °C, as the presence of jarosite would be revealed by the evolution of sulfur dioxide. Materials collected from the upper mine dump gave no sulfur dioxide but a very minor peak was detected in one of the samples from the lower mine dump. This sample and a small number of others taken from both dumps (to give a general mineralogical profile) underwent phase identification by XRD.

The lower mine dump materials typically contained quartz, jacobsite, anatase, montmorillonite, muscovite and illite. The only sulfate that could possibly fit the diffraction pattern for the sulfur dioxide generating sample was woodwardite \((\text{Cu}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12}\cdot2\cdot4(\text{H}_2\text{O}))\) but confidence in this interpretation was low. Though the woodwardite reference pattern could fit to the sample pattern peaks they could all be explained by the other phases present. The trace amounts of sulfur dioxide detected suggested that the sulfur bearing phase was at a very low abundance. The upper mine dump materials typically contained quartz, hemimorphite, smithsonite, anatase, illite and montmorillonite. The lack of detection of lead jarosite was unfortunate but the fact that potassium and sodium forms had been obtained meant that the project investigating cation variation could still continue. The jarosite-like colour observed across the Lake District sample site was likely due to montmorillonite, which was detected in all the samples collected at the mine and can have a similar colour to what was observed.
4.3 Synthesis of jarosite

Synthetic samples allow the thermal decomposition of jarosite to be analysed without the complicating influence of other mineral phases or organic compounds. The results of synthetic studies also aid the interpretation of complex natural mixtures, such as PRT and GS. Jarosite synthesis reactions typically involve the hydrolysis of ferric ions and the generation of sulfuric acid (Figure 4.5) (Dutrizac & Jambor, 2000).

\[
3\text{Fe}_2(\text{SO}_4)_3 + \text{Na}_2\text{SO}_4 + 12\text{H}_2\text{O} \rightarrow 2\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}_2\text{SO}_4
\]

Figure 4.5. The synthesis reaction for sodium jarosite (Dutrizac & Jambor, 2000).

Many different synthesis processes exist for jarosite but the method that was most feasible with the equipment available in the laboratory was that described by Basciano & Peterson (2008). On the 11th May 2013 the first attempt to synthesise sodium jarosite was carried out. The masses and volumes of the reagents were adjusted for the volume of the pressure vessel (described in Chapter 2). Ten g of ferric sulfate hydrate and 0.2125 g of sodium sulfate were added to the vessel and covered in 25 ml of water. The vessel was sealed and heated at 140 °C for 48 hours. The vessel headspace was not purged.

Upon opening the vessel there was a strong acidic smell and bright red crusts were seen on the vessel walls above the liquid. The water was drained into a beaker and was found to have become bright green with some solids floating within it. At the base of the bomb was a yellow slurry that was scooped out with a scalpel and dried in a 110 °C oven for half an hour. To rapidly check if this material was sodium jarosite Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy analysis of the material was used to produce an infrared spectrum, which was compared to published spectra for jarosite (Figure 4.6).
Chapter 4 – A quantitative study of the oxidising potential of jarosite in thermal experiments on Mars

The published spectra for jarosite, shown in Figure 4.6, are plotted with the y axis showing the intensity of the reflected infrared beam at different wavenumbers. The spectrum of the synthesised material collected from the pressure vessel is plotted with the y axis showing absorbance (with absorbance = \( \log_{10} \frac{1}{\text{intensity of reflected beam/ intensity of illuminating beam}} \)) plotted against wavenumber (Figure 4.6). Wavenumber is a measure of the number of wavelengths per centimetre. Though the y axis values will be altered when comparing intensity to absorbance peak position and relative peak height remain diagnostic.

The spectrum for the synthesised powder appears similar to published spectra for jarosite. The only significant difference is seen in the peaks attributed to the \( v_3 \) vibrational mode for sulfate, which are smaller and suggest some sort of minor compositional difference between the synthetic jarosite and the materials studied by Sasaki et al., (1998). The synthesis process was performing well, however the yield of jarosite was only 0.1 g. It was considered that the formation of iron oxide in the headspace of the vessel may have depleted iron and oxygen in the aqueous phase, which would impede jarosite formation. It was decided to make a second

![Figure 4.6. Infrared spectra for potassium jarosite (KJ) and sodium jarosite (NaJ) adapted from Sasaki et al., (1998), who analysed synthetic samples are shown on the left. The bonds and vibrational modes correlating to peaks at different wavenumbers are labelled, hydronium? Indicates O-H stretching inferred to be linked to hydronium in jarosite (Bishop & Murad, 2005; Sasaki et al., 1998; Spratt et al., 2013). The data from this study are shown on the right.](image-url)
attempt at jarosite synthesis and to increase the mass of reagents, the volume of liquid in the
vessel and to purge the headspace with argon.

On the 15\textsuperscript{th} May 2013 18 g of ferric sulfate hydrate was mixed with 0.3825 g of sodium sulfate
in the vessel and then covered in 45 ml of deionised water. The vessel was sealed, purged
with argon and then heated at 140 °C for 48 hours. Despite purging the headspace iron oxide
was still found coating the vessel walls above the liquid (Figure 4.7). However, after draining
the vessel substantially more yellow precipitate was seen on the vessel walls compared to the
first synthesis reaction. The precipitate was scraped and washed out into a beaker using a
spatula and deionised (DI) water and the powder allowed to settle out before being dried at
110 °C for half an hour.
In total 2.5 g of jarosite was synthesised. The powder was taken to the Natural History Museum and phase identification through XRD confirmed the material was sodium jarosite. Carphosiderite (the misnamed phase discussed in Chapter 3) was suggested by the X’Pert software as a possible match to the pattern for the synthetic material. Discussions with researchers at the Natural History Museum led to a collaboration and a request to supply them with a single crystal of sodium jarosite that could be used for XRD studies to improve the identification and structural interpretation of sodium jarosite. Optical microscopy was used to search the powder for a crystal large enough for a single crystal study but objects that initially appeared to be single crystals turned out to be agglomerations of very small particles.

It was decided to perform a third synthesis of jarosite and extend the synthesis time to increase crystal size and possibly increase the total yield of material. On the 26th June 2013 18 g ferric sulfate hydrate was mixed with 0.3825 g of sodium sulfate and covered in 45 ml of deionised water. The vessel was sealed but not purged as this was not successful in preventing the formation of iron oxide in the headspace in the previous synthesis experiment. The vessel was heated at 140 °C for eight days. When the vessel was opened it was found that no iron oxide had formed in the headspace and the fluid was a brown-yellow colour rather than green. 3 g of powder was collected. Phase quantification of the powder using XRD and Rietveld refinement found that the material was made up of sodium jarosite showing two distinct preferred orientations. This suggests that though the material was 100% sodium jarosite there was some compositional variation within the jarosite structure. The powder was searched for single crystals using optical microscopy. The longer synthesis time appeared to have increased crystal size in some instances though in general the majority of the powder remained very fine grained. Several candidates for single crystals were found and the best
(Figure 4.8) was used by the Natural History Museum in a study of the influence of temperature on the jarosite crystal lattice.

Potassium jarosite was synthesised using the method of Basciano & Peterson (2007), which is identical to that used to synthesise sodium jarosite other than sodium sulfate being replaced by potassium sulfate in the reagent mixture. This method was also extended to eight days to make the conditions as similar as possible to those used to precipitate sodium jarosite. The initial synthesis run was interrupted by a power cut so a second attempt was made on the 9th October 2013 with 18 g of ferric sulfate hydrate and 0.3825 g of potassium sulfate mixed with 45 ml of water and heated at 140 °C for eight days. The headspace was not purged.
Phase quantification of the powder removed from the vessel using XRD and Rietveld refinement found that 87% of the material was potassium jarosite with minor hydronium substitution but 12% appeared enriched in hydronium with lesser potassium, the remaining 1% was FeOH(SO$_4$). FeOH(SO$_4$) is known to form when water is lost from hydronium jarosite, a reaction that also produces amorphous iron hydroxide (Swayze et al., 2008). This water loss may have occurred during drying of the powder. The standard method for drying a sample is to heat the material in a 110 °C oven. This method was considered safe for the synthetic jarosite samples as water evolution does not begin to occur until 130 °C (Frost et al., 2005a). However, data examined after jarosite synthesis suggested that heating even at 110 °C causes hydronium to transfer protons to hydroxyl groups and convert both to water and the residual form of jarosite is similar to the more stable hydrothermal forms (Swayze et al., 2008). Swayze et al., (2008) recommend not heating jarosite above 60 °C, with experiments showing a reduction in unit cell dimensions and a 3.5 to 9% structural water loss during heating at 110 °C for 20 to 40 hours (Swayze et al., 2008). The synthetic samples were heated for approximately half an hour until the grains were dry, which would have minimized structural water loss but the stability of the synthetic jarosites may have been increased relative to most natural samples. The detection of FeOH(SO$_4$) in the synthetic potassium jarosite powder but not in sodium jarosite is likely related to the 12% hydronium enriched jarosite present in the former. This phase may have been present at a slightly greater abundance prior to heating but the fact it was not completely absent indicates drying for half an hour did not drive off all of the hydronium. The fluids removed from the pressure vessel after syntheses were found to be pH 1 and after the experiments were finished corrosion of the vessel interior was observed, particularly at the point of the water-headspace interface.
4.4 Lattice parameters of natural and synthetic jarosite samples

The unit cell of a mineral is the smallest group of atoms that possess the crystallographic symmetry and chemical properties of the mineral (Swayze et al., 2008). Substitutions of hydronium, potassium and sodium change the trigonal jarosite unit cell parameters in a linear fashion but many synthetic jarosites show some degree of zoning (Basciano & Peterson, 2007; Basciano & Peterson, 2008). The detection of a hydronium enriched phase and different preferred orientations suggests there was some degree of zoning in the materials synthesised in this project. Sample grinding and stirring were used to minimise heterogeneity in the powder. The synthetic sodium jarosite was labelled as SNa and the potassium jarosite as SK. Rietveld refinement of the jarosite unit cell when jarosite is present at an abundance of 5% or greater of a mixture allows the lattice parameters a and c to be inferred and the alkali to hydronium ratio estimated (Figure 4.9) (Table 4.1) (Basciano & Peterson, 2008).

![Figure 4.9. Unit-cell parameters a vs. c of the K-Na-H₂O jarosite series by Basciano & Peterson (2008). The data for this project are plotted and show the relative abundance of potassium, sodium and hydronium in each jarosite sample.](image-url)
Chapter 4 – A quantitative study of the oxidising potential of jarosite in thermal experiments on Mars

### Table 4.1. Unit cell parameters of jarosite phases

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unit cell lattice parameter a</th>
<th>Unit cell lattice parameter c</th>
<th>Estimated alkali to hydronium ratio*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRT</td>
<td>7.3135</td>
<td>17.077</td>
<td>80:20</td>
</tr>
<tr>
<td>GS</td>
<td>7.3230</td>
<td>16.662</td>
<td>80:20</td>
</tr>
<tr>
<td>SK**</td>
<td>7.3096</td>
<td>17.188</td>
<td>85:15</td>
</tr>
<tr>
<td>SNa</td>
<td>7.3296</td>
<td>16.739</td>
<td>65:35</td>
</tr>
</tbody>
</table>

**Lattice parameters of major phase (a 12% hydronium rich phase is present).

The unit cell parameters of GS and SNa indicate a complete absence of potassium. In contrast, PRT does not plot directly on any of the axes shown in Figure 4.9 indicating a mix of sodium, potassium and hydronium. Given that potassium jarosite is the most thermodynamically stable form these observations suggest the groundwaters circulating in the rocks in St. Oswald’s Bay were relatively poor in potassium at PRT and completely depleted in potassium at GS (Dutrizac & Jambor, 2000). The alkali to hydronium ratio for the major phase in SK matches reasonably well with the natural samples, but this is countered by the additional hydronium-rich phase and minor FeOH(SO₄).

### 4.5 Experimental parameters

#### 4.5.1 Pyrolysis-GC-MS

The thermal experiments conducted on the natural jarosite clay from Brownsea Island in Chapter 3 were performed using individual samples at 100 °C intervals between 400 °C and 1000 °C. This was to maximise the chance of observing an interaction between the decomposition products of jarosite and organic compounds. These experiments proved that oxidation of organic matter was occurring in the sample and was caused by oxygen released during the thermal decomposition of jarosite. In this chapter the results of experiments that are more similar to the evolved gas analyses carried out by instruments such as Curiosity’s...
Sample Analysis at Mars (SAM) and Phoenix’s Thermal and Evolved Gas Analyzer (TEGA) are described.

The thermal decomposition products of SK, SNa, PRT and GS were investigated using stepped pyrolysis. In this method each sample was first heated at 300 °C and then at increments of 50 °C up to 1000 °C. Before heating samples were crushed and stirred in a pestle and mortar to reduce sample heterogeneity and remove the influence of grain size differences on thermal decomposition. At each temperature step the gases produced during pyrolysis were analysed by gas chromatography-mass spectrometry (GC-MS) using a J&W GS-Q PLOT column. The peak areas for water, oxygen, carbon dioxide and sulfur dioxide were recorded at each temperature step and then normalised to the starting sample mass. As a result of the jarosite-rich nature of all of the samples approximately 1 mg of material was used, rather than the 4 mg used in the natural jarosite clay experiments, which was to prevent saturation of sulfur dioxide on the mass spectrometer. The J&W GS-Q PLOT column was used to separate and quantify carbon dioxide, sulfur dioxide and oxygen but was not suitable for the quantification of water. As the focus of these experiments was an improved understanding of the production of sulfur dioxide and oxygen during jarosite decomposition and the detection of any carbon dioxide produced by oxidation this limitation of the column was not deemed to be problematic. The Agilent Technologies 6890 gas chromatograph was coupled to the 5973 mass spectrometer. The gas chromatograph injector was held at 200 °C and operated in split mode (35:1) with a column flow rate of 2 mL min⁻¹. The gas chromatograph oven was held for five minutes at 35 °C and then ramped at a rate of 10 °C min⁻¹ to 200 °C, where it was held for 4 minutes. Mass spectra were acquired in the scan range 10-150 atomic mass units (amu).
4.5.2 Calibration and quantification

Calibration curves were constructed by injections of sulfur dioxide diluted in nitrogen, injections of air to calibrate oxygen and pyrolysis of sodium bicarbonate to quantify carbon dioxide. The different response factors for the mass spectrometer for carbon dioxide, water and oxygen were found by measuring the peak areas for equal masses of each species and then normalising the calibration curves to the different responses for the same mass. Each pyrolysis experiment was repeated three times and error bars were plotted as the standard deviation from the mean. Water was plotted as peak areas normalised to starting sample mass.

4.5.2 Additional materials

To aid the interpretation of results from the natural samples, laboratory standards of quartz, calcite, gypsum, potassium sulfate, magnesium sulfate and sodium sulfate were pyrolysed using the same stepped pyrolysis method used for the jarosite samples. Synthetic magnesite was also available in the laboratory. As these experiments were designed predominantly to aid interpretation they were only conducted once and error bars are not presented. For the jarosite samples and the laboratory standards cumulative production of carbon dioxide, sulfur dioxide and oxygen were plotted by summing the gas production at each temperature step.

A laboratory standard of polyethylene was used to investigate the direct influence of jarosite decomposition on the detection of organic compounds. Polyethylene is ideal for such an experiment as it thermally decomposes to release a series of alkanes, alkenes and dienes. Polyethylene was mixed with either the synthetic potassium jarosite or the synthetic sodium jarosite and pyrolysed at 500 °C or 650 °C. Jarosite was mixed with polyethylene at a ratio of 10:1. The 500 °C experiment was designed to test the organic compound response at the
highest possible temperature at which jarosite decomposition should be minimal. The 650 °C experiment was performed as there should be a strong response for organic matter at 650 °C. At the time the polyethylene and jarosite experiments were being carried out the Agilent Technologies 6890 gas chromatograph was unavailable so the CDS 5200 pyroprobe was connected to the Agilent Technologies 7890A gas chromatograph. The transfer line was set at 300 °C and the valve oven at 320 °C to attempt to prevent polyethylene degradation products being retained in the system. The gas chromatograph injector was held at 270 °C and operated at a split flow of 50:1 with a column flow rate of 1.1 mL min⁻¹. Separation was performed on a J&W DB-5MS UI column. The gas chromatograph oven was held at 40 °C for 2 minutes and then ramped to 310 °C at a rate of 10 °C/min, where it was held for 10 minutes. Mass spectra were acquired in the range 40-550 amu so that carbon dioxide and sulfur dioxide could be measured and provide evidence of any jarosite decomposition taking place and subsequent oxidation of organic matter.
4.6 Thermal decomposition of jarosite samples

The stepped pyrolysis profile for each jarosite sample is presented and described in the following sections (Figures 4.10-4.13). In Section 4.6.5 the natural and synthetic samples and potassium- and sodium-rich compositions are compared and assessed (Figure 4.14).

4.6.1 Thermal decomposition of synthetic potassium jarosite (SK)

![Figure 4.10. The stepped pyrolysis profile for synthetic potassium jarosite (SK). Triplicate experiments with error bars showing standard deviation. *Water is presented as peak area normalised to starting sample mass as the chromatography column used to quantify carbon dioxide, sulfur dioxide and oxygen was not suitable for quantifying water.]

4.6.1.1 Sulfur dioxide

The first detection of sulfur dioxide was made at 500 °C when the sulfate ions within jarosite began to decompose (Frost et al., 2005a). Sulfur trioxide was not detected indicating it was breaking down instantaneously to give sulfur dioxide and atomic oxygen. Thermogravimetric
studies show that low-temperature dehydration reactions during jarosite decomposition lead to an alkali iron sulfate that decomposes to give sulfuric acid (if hydronium is present), ferric sulfate and an alkali sulfate (Frost et al., 2005a; Frost et al., 2006a; Lakshman et al., 2014). Sulfuric acid was not detected in the pyrolysis products, like sulfur trioxide it was rapidly decomposing at high temperatures. Sulfur dioxide production peaked at 700 °C at approximately 1 µmol produced per mg of potassium jarosite. Sulfur dioxide production then rapidly declined to background levels with increasing temperatures indicating the potassium sulfate produced during decomposition was stable up to at least 1000 °C during stepped pyrolysis.

4.6.1.2 Oxygen

Oxygen was first detected at 550 °C and its overall production profile correlated well with that of sulfur dioxide. Oxygen production peaked at 700 °C at approximately 0.5 µmol released per mg of synthetic potassium jarosite. Oxygen then rapidly declined to background levels with increasing temperature. These observations prove that jarosite decomposition produces substantial amounts of oxygen. The sulfur trioxide from sulfate degradation was clearly decomposing rapidly to give sulfur dioxide and atomic oxygen. This atomic oxygen appears to have then combined to form molecular oxygen and an SO₂:O₂ ratio of 2:1. If sulfur dioxide is not accompanied by oxygen during pyrolysis of a jarosite containing sample then it must be questioned at to what process or processes have consumed the oxygen.

4.6.1.3 Carbon dioxide

Carbon dioxide was released at low levels at every temperature step suggesting that the sample had very low levels of organic compound contamination. A carbonate phase would
not be present within the sample as the sample was synthesised under highly acidic conditions and any carbonate phase would break down at only high temperatures.

4.6.1.4 Water

From the first heating step at 300 °C, water was detected as a relatively high peak. This was due to water loss caused by dehydroxylation of the jarosite structure below 600 °C and before the onset of major sulfate decomposition and sulfur dioxide and oxygen production (Frost et al., 2005a). Water release showed a slight rise from 700 °C to 1000 °C. The origin of this high temperature water is uncertain, it was not accompanied by a rise in sulfur dioxide, which indicates that it is not related to the decomposition of iron sulfate or sulfuric acid. The water may well be related to the nature of stepped pyrolysis experiments. After being heated at a temperature step, the sample is sat in the pyrolysis oven at an isothermal temperature while the GC-MS analysis is performed. During this period the sample may have become hydrated if any water remained in the system. The potassium sulfate formed by jarosite decomposition may have repeatedly gained and lost water during the cycles of heating and waiting at an isothermal temperature.
4.6.2 Thermal decomposition of synthetic sodium jarosite (SNa)

![Graph showing gas production and water peak area vs. temperature.](image)

**Figure 4.11.** The stepped pyrolysis profile for synthetic sodium jarosite (SNa). Triplicate experiments with error bars showing standard deviation. *Water is presented as peak area normalised to starting sample mass as the chromatography column used to quantify carbon dioxide, sulfur dioxide and oxygen was not suitable for quantifying water.*

### 4.6.2.1 Sulfur dioxide

Sulfur dioxide was first detected at 650 °C and rose rapidly to peak at 800 °C before falling to background levels by 950 °C. Variation between repeat analyses was greater than with SK despite equivalent grinding and stirring of the sodium jarosite powder. This suggests that the two preferred orientations detected through XRD indicate two slightly different forms of sodium jarosite with possible variances in hydronium substitution. Sulfur dioxide peak production was 0.8 µmol per mg of sodium jarosite. The production of sulfur dioxide indicates decomposition of the hydronium and ferric sulfate components within the jarosite (Frost et al., 2005a). As with SK, the alkali sulfate formed during sodium jarosite decomposition
appears to be stable up to at least 1000 °C as no high temperature rise in sulfur dioxide production was observed.

### 4.6.2.2 Oxygen

Oxygen was first detected at 650 °C and its production profile correlated well with sulfur dioxide, with a peak in production at 800 °C of approximately 0.4 µmol per mg of sodium jarosite. The oxygen was clearly related to sulfur dioxide production and proved that sodium jarosite also releases oxygen during thermal decomposition via sulfate decomposition. Sulfur trioxide was not detected indicating its rapid breakdown into sulfur dioxide and atomic oxygen.

### 4.6.2.3 Carbon dioxide

Carbon dioxide was present at very low levels at every temperature step suggesting very minor contamination by organic compounds. As with potassium jarosite carbonate is not considered a possibility because i) the material was synthesised in a fluid with a pH of 1 and ii) carbonate would only break down at high temperatures.

### 4.6.2.4 Water

Water peaked at 500 °C due to the loss of hydroxyl groups from jarosite before the onset of sulfate decomposition (Frost et al., 2005a). A high-temperature water release was seen that initiated at 850 °C. Again the origin of this high-temperature water production is uncertain but it is attributed to hydration of the sodium sulfate formed through sodium jarosite decomposition during the waiting period between temperature steps.
4.6.3 Thermal decomposition of a natural potassium jarosite rich sample (PRT)

Sulfur dioxide was first detected at 500 °C and peaked at 600 °C before rapidly declining to background levels by 750 °C. PRT consists of 42% potassium jarosite and 58% quartz so the only possible source of sulfur dioxide is the potassium jarosite. Peak sulfur dioxide production was approximately 0.4 µmol per mg of sample. This value fits well with the observation that the synthetic potassium jarosite sample produced approximately 1 µmol of sulfur dioxide per mg of sample. The alkali sulfates formed through jarosite decomposition appeared stable up to 1000 °C in the natural sample as no further rise in sulfur dioxide was seen.

Figure 4.12. The stepped pyrolysis profile for the natural potassium jarosite rich sample (PRT). Triplicate experiments with error bars showing standard deviation. *Water is presented as peak area normalised to starting sample mass as the chromatography column used to quantify carbon dioxide, sulfur dioxide and oxygen was not suitable for quantifying water. The m/z 28 peak is labelled as CO? as it is inferred to be carbon monoxide as discussed in the text.
4.6.3.2 Oxygen

Oxygen was not detected at any temperature step. Observations from the synthetic samples indicated that a production of approximately 0.2 µmol of oxygen per mg of sample would be expected to accompany peak sulfur dioxide production at 600 °C. A reaction that consumes oxygen must have been occurring during stepped pyrolysis. For PRT it is inferred that oxidation of organic matter consumed oxygen released by jarosite decomposition.

4.6.3.3 Carbon dioxide

Carbon dioxide shows a broad peak that achieves a maximum at 600 °C but has a significant shoulder centred around 400-450 °C. This low-temperature shoulder precedes the onset of sulfate decomposition and it is attributed to the decarboxylation of organic matter as a carbonate is unlikely to be present in this material and decarboxylation was seen in the natural jarosite clay experiments conducted in Chapter 3. The peak seen at 600 °C is attributed to carbon dioxide forming through the oxidation of organic matter.

4.6.3.4 Carbon monoxide

A m/z 28 peak was detected from 400 °C and above. It is interpreted to be carbon monoxide rather than nitrogen as it was not detected in any other sample and was not present at every temperature. It also shows a degree of correlation with carbon dioxide and sulfur dioxide as it shows a slight peak at 600 °C.

4.6.3.5 Water

As with the synthetic jarosite samples PRT produced a low-temperature water peak, which is attributed to hydroxyl loss from potassium jarosite. The peak is not as sharp as that seen in the synthetic samples but a natural jarosite containing potassium, sodium and hydronium is
likely to be significantly more complex and less crystalline. Water production drops up to 600 °C and then shows a slight increase with temperature.

4.6.4 Thermal decomposition of a natural sodium jarosite rich sample (GS)

![Graph showing gas production vs temperature for a natural sodium jarosite rich sample (GS).](image)

Figure 4.13. The stepped pyrolysis profile for a natural sodium jarosite rich sample (GS). Triplicate experiments with error bars showing standard deviation. *Water is presented as peak area normalised to starting sample mass as the chromatography column used to quantify carbon dioxide, sulfur dioxide and oxygen was not suitable for quantifying water.

### 4.6.4.1 Sulfur dioxide

The first detection of sulfur dioxide was made at 550 °C with peak production observed at 600 °C. Unlike the other samples there was a slight increase in sulfur dioxide at higher temperatures, starting at 800 °C. Sodium sulfate is thought to be stable until very high temperatures so it is unlikely that the sodium sulfate formed through sodium jarosite decomposition was the cause. Gypsum is present in the sample but calcium sulfate is also
very stable below 1000 °C. Combined with the observations for carbon dioxide (section 4.6.4.3) it appears that there may be components in GS that are X-ray amorphous and require further experiments to identify.

4.6.4.2 Oxygen

GS showed a high temperature evolution of oxygen that increased with sulfur dioxide. The amount of oxygen detected was very low but it suggests at this temperature all the possible sinks for oxygen had been exhausted. Oxidation, thermal decomposition and volatilisation of organic matter at lower temperatures means that little to none is present at 1000 °C.

4.6.4.3 Carbon dioxide

GS showed the greatest production of carbon dioxide for any of the samples. From 350 °C carbon dioxide production rapidly increased and peaked at 600 °C at over twice the peak height of sulfur dioxide. A high-temperature shoulder was seen at 800 °C before carbon dioxide rapidly decreased to low levels. The shoulder can be explained by the presence of calcite, which was identified by XRD. Oxidation of organic matter is highly unlikely to be the primary cause of the 600 °C carbon dioxide peak. The presence of another carbonate is the best explanation. The co-location of jarosite and carbonate in a sample (with jarosite forming from a potassium depleted fluid that formed only sodium jarosite) is evidence that pyrite oxidation and jarosite formation occurred over a very small area and likely rapidly. Such conditions may have increased the probability for amorphous phases to be present. In a system like the acidic stream from which PRT was sampled jarosite forming conditions are much more stable and long lasting and would lead to more crystalline phases.
4.6.4.4 Water

Water peaked at 450 °C and was relatively constant at higher temperatures. Dehydroxylation of jarosite, water loss from gypsum and any potential hydrated amorphous phases were the probable sources.

4.6.5 Comparison of jarosite samples

![Comparison of stepped pyrolysis profiles for the jarosite samples. *Water cannot be quantified with the GC column used to quantify carbon dioxide, sulfur dioxide and oxygen so is presented as peak area normalised to sample mass.](Image)

*Figure 4.14. Comparison of stepped pyrolysis profiles for the jarosite samples. *Water cannot be quantified with the GC column used to quantify carbon dioxide, sulfur dioxide and oxygen so is presented as peak area normalised to sample mass.*
Both synthetic and natural jarosite samples exhibit a trend where potassium jarosite begins to decompose to give sulfur dioxide at a lower temperature than sodium jarosite. In the synthetic samples the difference was 150 °C while in the natural samples potassium jarosite showed a small sulfur dioxide peak at 500 °C while the first detection for GS was made at 550 °C. The synthetic samples showed peak sulfur dioxide differing by 100 °C while PRT and GS peaked at 600 °C. These observations suggest that at the standard temperature for the pyrolysis of macromolecular organic matter (around 600 °C) differences between potassium and sodium jarosite thermal decomposition will be minimal. However, pyrolysis at the lower temperature of 500 °C for a sample containing sodium jarosite may produce significantly less oxidising conditions than a potassium jarosite sample heated at the same temperature. It was stated in Section 4.3 that drying of the synthetic jarosite samples may have inadvertently increased their stability. Increased stability would be a good explanation for the higher decomposition temperatures and greater difference between synthetic potassium and sodium jarosite thermal decomposition. The most important observation when comparing the four stepped pyrolysis profiles is that synthetic jarosite samples produced peak oxygen at the same temperature as peak sulfur dioxide and the amount of oxygen produced is about half that of sulfur dioxide. In both natural samples this oxygen was absent. It was likely consumed in oxidising reactions that would hinder the detection of organic compounds.

Peak water production appears to shift in temperature with different forms of jarosite. In samples that have a low number of phases and contain jarosite as a major phase this may be supporting evidence for different forms of jarosite. For example, if a rover thermally analysed several jarosite-bearing layers within a rock sequence and found sulfur dioxide and water peaks shifted between samples it would be possible evidence for cation variation between
the layers. These observations would suggest the individual layers formed from different fluids or a source with variable potassium and sodium concentrations through time.

Both natural samples show a peak in carbon dioxide with sulfur dioxide but interpreting this as evidence of organic matter oxidation is far from simple. In PRT (Figure 4.14c) carbonate is known to be absent from the sample and the peak of carbon dioxide is inferred to be related to carbon compound oxidation. GS (Figure 4.14d) is carbonate bearing and appears to contain calcite and an amorphous carbonate that breaks down at 600 °C, the same temperature as peak sulfur dioxide release. To relate carbon dioxide and sulfur dioxide in natural samples with jarosite decomposition and oxidation of organic matter with confidence relies on the absence of carbonates in the sample.

4.7 Thermal decomposition of laboratory standards

GS is a complex sample that requires a suite of techniques to attempt to fully understand its mineralogy. XRD suggested the presence of calcite, gypsum, sodium jarosite and quartz but an analogue mixture of lab standards and synthetic sodium jarosite does not show a comparable stepped pyrolysis profile to that of GS, particularly for the major carbon dioxide peak at 600 °C (Figure 4.15). An amorphous carbonate phase and amorphous sulfate phase that decompose at high temperatures were inferred to be present. Magnesium carbonate and magnesium sulfate were added to the analogue mixture and the resulting stepped pyrolysis profile was much closer to that seen in GS, a carbon dioxide peak was seen at 600 °C and a high-temperature sulfur dioxide and oxygen rise was seen. When comparing untreated and acid-washed subsamples of GS an increase in sulfur dioxide was seen in the acid-washed sample (Section 4.2.1). The sulfur dioxide increase suggests the presence of carbonate was somehow suppressing the generation of sulfur dioxide. It is important to
consider that in the acid treatment study the sample was pyrolysed straight at 1000 °C rather than through stepped pyrolysis, this would maximise the chance of sulfate decomposition being influenced by carbonate decomposition.

Figure 4.15. Laboratory standards and synthetic magnesite were used to better understand results from the jarosite samples. *Water is presented as peak area normalised to sample mass as discussed earlier in the chapter. **Fig. 4.16a shows laboratory standards mixed in the same proportion of phases identified by XRD. *** Fig. 4.16b shows the same mixture but with 0.1 mg of magnesium carbonate and 0.1 mg of magnesium sulfate added to see if these phases could be the amorphous phases inferred to be present in GS by stepped pyrolysis results.
Comparing Figure 4.15a with Figure 4.15g gives further evidence for an interaction between carbonates and sulfates during thermal decomposition. In Figure 4.15g calcite begins to decompose from 600 °C and carbon dioxide peaks at 800 °C. In Figure 4.15a the carbon dioxide peak appears suppressed when sulfur dioxide is at a maximum and begins to rise as sulfur dioxide declines. The sulfur dioxide peak was also much broader than it was during pyrolysis of the synthetic sodium jarosite on its own. However, when comparing Figure 4.15b with Figure 4.15h the carbon dioxide peak produced by magnesite appears unchanged when added to the mixture. In this experiment the calcite carbon dioxide peak matched that seen in Figure 4.15g. Sodium jarosite decomposed to give sulfur dioxide at a lower temperature than when pyrolysed on its own suggesting magnesite decomposition may have lowered jarosite decomposition temperature. The water peak in Figure 4.15b is seen to shift to lower temperatures mirroring the decreased jarosite decomposition temperature. This shift suggests that in hypothetical analyses of jarosite containing rock layers on Mars the presence of carbonate would significantly complicate interpretations about cation content and the presence of organic compounds. The lower breakdown temperature of sodium jarosite means that the production of sulfur dioxide and calcium carbonate decomposition do not overlap and the two appear to not influence each other. The interaction between sulfates and carbonates is explored further in the next section and Figure 4.16 and Table 4.2.

Gypsum, potassium sulfate and sodium sulfate produced no sulfur dioxide during stepped pyrolysis up to 1000 °C. Of the sulfate laboratory standards tested only magnesium sulfate produced sulfur dioxide and oxygen from 850 °C. Such a high temperature of decomposition would be unlikely to interfere significantly with the detection of organic matter.
The majority of samples show an increase in water release with temperature. This was one of the observations from the synthetic jarosite samples that was difficult to explain. The temperature profiles from the laboratory standards suggest that this water evolution was related to the experimental procedures. In stepped pyrolysis-GC-MS experiments the samples are pyrolysed and then kept at an isothermal temperature in the pyrolysis oven while the GCMS analysis is carried out. During this period it is possible that any water remaining in the oven from pyrolysis is reabsorbed onto the sample and is then released during the next pyrolysis experiment.

### 4.8 Cumulative production of gases during the breakdown of sulfates and lab standards

![Cumulative gas production](Image)

**Figure 4.16.** Cumulative production of gases during stepped pyrolysis of jarosite samples and laboratory standards.
Table 4.2. Cumulative values of gas produced during stepped pyrolysis

<table>
<thead>
<tr>
<th>Ref. no.</th>
<th>Sample</th>
<th>CO$_2$ detected (μmol/mg)</th>
<th>SO$_2$ detected (μmol/mg)</th>
<th>O$_2$ detected (μmol/mg)</th>
<th>Ratio of SO$_2$ to O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Synthetic K jarosite</td>
<td>0.170 ± 0.01</td>
<td>2.420 ± 0.06</td>
<td>1.050 ± 0.06</td>
<td>1:0.43</td>
</tr>
<tr>
<td>(2)</td>
<td>Synthetic Na jarosite</td>
<td>0.134 ± 0.04</td>
<td>1.935 ± 0.12</td>
<td>0.930 ± 0.12</td>
<td>1:0.48</td>
</tr>
<tr>
<td>(3)</td>
<td>Natural K jarosite rich sample</td>
<td>0.821 ± 0.20</td>
<td>0.925 ± 0.22</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(4)</td>
<td>Natural Na jarosite rich sample</td>
<td>1.300 ± 0.079</td>
<td>0.162 ± 0.068</td>
<td>0.003 ± 0.005</td>
<td>1:0.02</td>
</tr>
<tr>
<td>(5)</td>
<td>Lab standards analogue to (4)</td>
<td>0.756</td>
<td>0.453</td>
<td>0.224</td>
<td>1:0.49</td>
</tr>
<tr>
<td>(6)</td>
<td>Analogue (5) plus MgCO$_3$&amp;MgSO$_4$</td>
<td>1.673</td>
<td>0.356</td>
<td>0.186</td>
<td>1:0.52</td>
</tr>
<tr>
<td>(7)</td>
<td>Gypsum</td>
<td>0.049</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(8)</td>
<td>K sulfate</td>
<td>0.011</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(9)</td>
<td>Mg sulfate</td>
<td>0.113</td>
<td>0.290</td>
<td>0.141</td>
<td>1:0.49</td>
</tr>
<tr>
<td>(10)</td>
<td>Na sulfate</td>
<td>0.140</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(11)</td>
<td>Calcite</td>
<td>8.219</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(12)</td>
<td>Magnesite</td>
<td>7.446</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(13)</td>
<td>Quartz</td>
<td>0.004</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Both of the synthetic jarosite samples show significant sulfur dioxide production during stepped pyrolysis between 300 °C and 1000 °C. Oxygen is produced at approximately half the amount of sulfur dioxide. The data proves that jarosite is highly oxidising during high-temperature pyrolysis experiments. Oxygen from sulfate decomposition is not consumed by other reactions occurring during the decomposition of the jarosite structure and it is free to react with organic compounds or other species. The synthetic potassium jarosite sample produced more sulfur dioxide and oxygen than the synthetic sodium jarosite. Analysis of the lattice parameters in Section 4.4 suggested that sodium jarosite was more enriched in hydronium overall relative to the major phase seen in the potassium jarosite sample. However, the potassium jarosite powder also contained a hydronium-enriched jarosite phase that made up 12% of the powder and 1% FeOH(SO$_4$). With these phases being present the hydronium content of the potassium jarosite powder is slightly greater than that of the
sodium jarosite powder. A good understanding of jarosite decomposition requires the use of XRD. The Chemistry and Mineralogy (CheMin) instrument on MSL will be extremely useful in interpreting Evolved Gas Analysis (EGA) results from materials in which jarosite is a phase.

In the natural jarosite rich samples sulfur dioxide was produced during decomposition but oxygen was absent. The very minor oxygen peak seen in GS is inferred to be related to an amorphous magnesium sulfate phase, which broke down at high temperatures. Reactions, including the oxidation of organic matter, must have consumed the oxygen resulting from jarosite decomposition. The mix of laboratory standards designed to represent the mixture of phases detected by XRD of GS does not represent the cumulative production of gases by GS well. GS showed a greater carbon dioxide production and lower sulfur dioxide production than the analogue mixture of standards. The synthetic sodium jarosite had a greater hydronium content than the sodium jarosite in GS, which would explain the greater production of sulfur dioxide. The presence of an amorphous carbonate phase (identified through stepped pyrolysis) would explain why the analogue mixture does not match GS’s carbon dioxide production. The analogue mixture with added magnesium carbonate and magnesium sulfate shows a more similar, though slightly greater, cumulative production of carbon dioxide.

The unusual relationship that was being seen between sulfur dioxide and carbon dioxide production when jarosite was mixed with carbonates can be explored further by studying the cumulative gas production of each species. The total amount of sulfur dioxide produced by the analogue mixture was around 23% of that detected in the single phase synthetic sodium jarosite, this shows that sulfur dioxide was not consumed during pyrolysis as it made up a quarter of the analogue mixture. The amount of carbon dioxide produced by the analogue
mixture was 9% of that detected in the single phase heating of the calcite laboratory standard, again a value that is extremely similar to the 7% abundance of calcite in the analogue mixture. This shows that neither sulfur dioxide or carbon dioxide were consumed by any secondary reactions in the analogue mixture, rather their decomposition temperatures were changing slightly, suggesting some sort of thermodynamic effect of mixing is the cause. The carbon dioxide produced by the analogue mixture with additional magnesium carbonate and magnesium sulfate shows no depletion from what would be expected from the proportion of carbonates in the sample. However, sulfur dioxide appears depleted, being present at only around 70% of what would be expected from the analogue mixture plus magnesium carbonate and magnesium sulfate. The thermal decomposition of carbonates is an endothermic process, with calcium carbonate decomposition being more endothermic than magnesium carbonate decomposition. This could explain why the decomposition of sodium jarosite was higher than expected when mixed in the analogue mixture to GS. However, endothermic reactions do not explain why jarosite broke down at a lower temperature and produced less sulfur dioxide when present in the analogue mixture with additional magnesium carbonate and magnesium sulfate. Heterogeneity in the sodium jarosite powder is inferred as the probable cause.

Gypsum, potassium sulfate, sodium sulfate and quartz were all essentially blank runs as only very low levels of carbon dioxide were detected during stepped pyrolysis. The low levels of cumulative carbon dioxide production seen indicate the experimental procedure did not introduce any significant contamination. A slightly greater carbon dioxide production was seen in the synthetic jarosite samples, this was likely related to contamination during synthesis. The pressure vessel was cleaned by performing water only cycles before synthesis
Chapter 4 – A quantitative study of the oxidising potential of jarosite in thermal experiments on Mars

but previous experiments conducted in the instrument included experiments with oils and shales that would leave behind a minor organic residue in the vessel.

4.9 Pyrolysis of polyethylene and synthetic jarosite samples

The availability of synthetic samples allows the interaction between oxygen from jarosite decomposition and organic compounds to be studied directly (Figure 4.17).

![Chromatograms showing the thermal decomposition products of samples of polyethylene and 10:1 mixtures of sodium jarosite and polyethylene at 500 °C and 650 °C. The chromatograms on the right highlight the behaviour of C_{11} compounds at the different conditions; a: undecane, b: 1-undecene, c: 1-10-undecadiene.](image_url)
Polyethylene was selected as it thermally decomposes to give a series of alkanes, alkenes and dienes. The chromatograms are shown for only the first 25 minutes of the GC run as all of the peaks were detected in this period.

Pyrolysis of polyethylene at 500 °C produced a series of weak peaks for alkanes and alkenes. Pyrolysis of polyethylene at 650 °C produced a series of peaks for alkanes, alkenes and dienes. The alkane and alkene peaks were significantly greater than at 500 °C, particularly for the alkenes. Very small peaks for benzene and toluene were also seen at 650 °C.

Pyrolysis of the 10:1 sodium jarosite and polyethylene mixture at 650 °C produced a series of peaks with many appearing significantly reduced relative to the polyethylene only experiment. The peaks are not affected uniformly, the diene and alkene peaks are much reduced but the alkane peaks did not change significantly. The peaks for benzene and toluene were increased relative to the polyethylene only experiment at 650 °C. At 500 °C the 10:1 sodium jarosite and polyethylene mixture produced slightly stronger peaks for alkanes and alkenes than in the polyethylene only mixture, minor peaks for benzene and toluene were also detected.

These results illustrate that oxidation of organic matter by oxygen from jarosite decomposition not only reduces the response for organic matter but also selectively targets compounds with double bonds. Jarosite reduces the chance of detecting organic matter in thermal experiments and complicates any response that is detected. However at 500 °C the presence of jarosite appeared to slightly increase the response for organic matter.
The 10:1 mixtures of potassium jarosite and polyethylene showed a similar behaviour to the sodium jarosite experiments (Figure 4.18).

Figure 4.18. Chromatograms showing the thermal decomposition products of samples of polyethylene and 10:1 mixtures of potassium jarosite and polyethylene at 500 °C and 650 °C. The chromatograms on the right highlight the behaviour of $C_{11}$ compounds at the different conditions; a: undecane, b: 1-undecene, c: 1-10-undecadiene.
The potassium jarosite mixture’s response at 500 °C was slightly greater for alkanes and alkenes than in the polyethylene only experiment. At 650 °C the response for dienes and alkenes in the mixture were reduced while alkanes were largely unchanged. However, the response for organic matter was greater when polyethylene was mixed with potassium jarosite relative to sodium jarosite at 650 °C (Figure 4.19).

Figure 4.19. The peak areas for benzene, toluene, alkanes, alkenes and dienes detected during pyrolysis of polyethylene and polyethylene and jarosite mixtures during pyrolysis at 500 °C and 650 °C.
This was unexpected as the potassium jarosite was seen to produce greater amounts of sulfur dioxide and oxygen during thermal decomposition than the sodium jarosite sample. This result implies that the sodium jarosite sample was more oxidising in these experiments. However, an analysis of the sulfur dioxide and carbon dioxide produced during pyrolysis reveals that this does not appear to be the case (Figure 4.20).

![Figure 4.20. Sulfur dioxide and carbon dioxide production during pyrolysis of polyethylene (P), potassium jarosite (KJ), sodium jarosite (NaJ) and 10:1 mixtures of jarosite and polyethylene at 500 °C or 650 °C. *The peak areas are normalised to the starting mass of jarosite or polyethylene.](image)

At 650 °C both 10:1 mixtures saturated the mass spectrometer for sulfur dioxide but the mixture containing potassium jarosite produced a somewhat greater peak area for carbon dioxide. This indicates that more oxidation was occurring in the potassium jarosite mixture, which fits with the observations from the cumulative gas production (Figure 4.16). It is
inferred the reason for a greater response for organic matter with the potassium jarosite mixture is instrumental. In blank runs it was observed that some residues of organic matter were accumulating in the instrument during the week the experiments were carried out. The sodium jarosite experiment was one of the first conducted whereas the potassium jarosite mixture was investigated several days later. During experimentation polyethylene was found to periodically cause blockages in the pyrolysis unit.

Though Figure 4.19 helped to resolve some of the complications from the polyethylene experiment the most significant observation from the data is that the presence of organic matter appears to dramatically accelerate the decomposition of jarosite. When mixed with polyethylene the production of sulfur dioxide from jarosite is much greater at both temperatures. It suggests that under these experimental conditions pyrolysis of polyethylene was exothermic and may have encouraged jarosite decomposition. In the glass processing industry the presence of carbon is found to lower the decomposition temperature of sulfates by reactions that form carbon monoxide (Samadhi et al., 2003), so polyethylene may also have been reacting with jarosite in some way.
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4.10 Pyrolysis of natural samples - searching for organic matter

Following the observation that the occurrence of jarosite decomposition at 500 °C appeared to slightly increase the response for organic compounds PRT and GS were pyrolysed at both 500 °C and 650 °C (Figure 4.21).

Figure 4.21. Peaks for acetic acid, benzene and toluene produced through pyrolysis of the natural samples GS and PRT. All chromatograms are presented at the same scale.
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The major peaks for GS and PRT were carbon dioxide and sulfur dioxide, the only organic compounds detected were acetic acid, benzene and toluene in PRT and a very minor peak for benzene in GS. Comparisons between the detected amounts of these three organic compounds at the different temperatures shows there is relatively little difference between pyrolysis at 500 °C and 650 °C for PRT. GS appears to be very poor in organic matter that can be sampled by thermal experiments so it is not possible to compare the difference between pyrolysis at 500 °C and 650 °C for this sample. The observation that jarosite decomposition during pyrolysis at 500 °C may increase the response for organic matter appears to be possibly demonstrated during pyrolysis of PRT. However, this hypothesis would require substantial testing that is beyond the scope of this project before this becomes a certainty.

4.11 Implications and discussion

The results presented in this chapter conclusively prove that the thermal decomposition of jarosite results in a substantial release of oxygen into pyrolysis chambers. In synthetic jarosite samples it was found that oxygen is produced at half the amount of sulfur dioxide. This ratio of two sulfur dioxide molecules for every one oxygen molecule indicates that there was no consumption of oxygen in other decomposition reactions occurring in the jarosite structure (i.e. dehydroxylation and water loss). In all the natural samples tested the oxygen associated with jarosite decomposition was not detected indicating it was consumed in oxidising reactions.

Stepped pyrolysis of jarosite is characterised by a spike in water production below 600 °C and then a substantial high temperature spike of sulfur dioxide that is associated with oxygen in synthetic samples and with elevated levels of carbon dioxide in natural samples. The position of the water and sulfur dioxide peaks appears to shift with different jarosite structures,
potassium jarosite will begin to break down at a lower temperature than sodium jarosite for example. However, shifts in these peaks could only be interpreted with confidence with supporting evidence from XRD and in very simple mixtures. The more phases that are present in a sample the more complex the interactions in the mixture. In this work the presence of carbonates and polyethylene appeared to influence jarosite decomposition temperatures. Jarosite itself was found to not only reduce the response for organic compounds in thermal experiments but to selectively oxidise double bonds thereby complicating interpretations of chromatograms.

Synthesising jarosite that is representative of what is seen in most natural samples appears to be challenging. The samples produced in this project were found to be more analogous to relatively stable hydrothermal forms of jarosite and broke down at higher temperatures than PRT and GS, which were formed at low temperatures. Any future studies focusing on the behaviour of sedimentary jarosite would need to consider how best to synthesise a synthetic analogue and consider the influence of crystalline or amorphous phases present in natural mixtures.

Sulfur dioxide was first detected during in situ evolved gas analysis (EGA) on Mars when the Rocknest samples were analysed by Curiosity (Figure 4.22) (McAdam et al., 2014). The oxidation of sulfides and the decomposition of iron sulfates were suggested as the possible sources (Leshin et al., 2013). The profiles for sulfur dioxide produced by the Rocknest samples appear remarkably similar to the profiles seen for the synthetic jarosite samples in showing a low initial sulfur dioxide production and then a more substantial peak with increasing temperature. The large carbon dioxide peak present at the onset of sulfur dioxide evolution was interpreted to be related to the decomposition of a fine grained iron or magnesium
carbonate (Leshin et al., 2013). However, it is possible that there could have been a minor contribution from the oxidation of organic matter.

The large high-temperature sulfur dioxide peak seen in Rocknest is accompanied by very low levels of carbon dioxide suggesting oxidation of organic matter was not occurring though oxygen was also at background levels (Leshin et al., 2013). If this sulfur dioxide is related to the decomposition of an iron sulfate then the missing oxygen still has to be accounted for, the oxidation of sulfide phases would be a possible explanation. The temperature profile for the Rocknest sulfur dioxide would suggest a jarosite phase that is very stable and possibly hydrothermal. The aeolian Rocknest material is a complex mixture of phases with a large amorphous component and possible carbonate (Bish et al., 2013; Leshin et al., 2013). This complexity means that attempting to infer the structure and stability of jarosite from EGA data is extremely challenging. Windblown material on Mars contains many phases and

Figure 4.22. Water, carbon dioxide, oxygen and sulfur dioxide production from the Rocknest samples (Leshin et al., 2013).
produces an extremely complex EGA profile so making interpretations about the structure of jarosite would only be possible through analysis by CheMin if jarosite was more abundant. The John Klein and Cumberland samples from the Sheepbed mudstone produced very broad high temperature sulfur dioxide peaks at significantly lower levels than seen in Rocknest (Ming et al., 2014). The environment preserved by the Sheepbed mudstone would have been highly unlikely to form jarosite and oxidation of sulfides is a more realistic explanation (Ming et al., 2014).

The Confidence Hills sample drilled from the Pahrump Hills at the base of Mount Sharp was found to contain jarosite, which was interpreted as evidence of acid-sulfate alteration (Figure 4.23) (Rampe et al., 2015). EGA produced a sulfur dioxide peak that began to rise at around

![Graph showing major volatiles released from the Confidence Hills sample.](image)

**Figure 4.23.** Major volatiles released from the Confidence Hills sample, estimated profiles are used for carbon dioxide, water and sulfur dioxide as the major isotopes saturated the mass spectrometer detector so minor isotopes were used to estimate signal (Franz et al., 2015).
520 °C and peaked at 600 °C but exhibited a substantial shoulder and a further small peak on top of this shoulder at 800 °C (Franz et al., 2015). Each sulfur dioxide peak was accompanied by a smaller oxygen peak and the sulfur dioxide and oxygen peaks at 800 °C were accompanied by a broad carbon dioxide peak (Franz et al., 2015). The temperature of release for sulfur dioxide would suggest a more sodium-enriched, potassium-poor jarosite phase. The presence of a sulfur dioxide shoulder does not fit any of the jarosite decomposition trends seen in this project. One possibility is that amorphous sulfide phases were present in the Confidence Hills sample, which were oxidised by jarosite decomposition and slowly decomposed to give sulfur dioxide. However, the oxygen levels are seen to correlate with sulfur dioxide extremely well, which suggests the shoulder is related to an amorphous sulfate phase. The slight peak at 800 °C appears unlikely to be related to jarosite decomposition as intermediate potassium or sodium sulfate should not break down below 1000 °C. As with GS it is inferred that Confidence Hills contains some amorphous magnesium sulfate.

Carbon dioxide appears low at 600 °C when jarosite decomposition is at its peak (Franz et al., 2015). Carbonate decomposition is a possible explanation but Confidence Hills was drilled from a rock that has experienced acidic alteration. A carbonate phase being present is therefore somewhat unlikely. If the observed carbon dioxide was related to organic matter oxidation caused by magnesium sulfate decomposition, rather than jarosite decomposition, it would suggest that a proportion of the organic matter present at Confidence Hills is extremely refractory and difficult to analyse. Currently data from Confidence Hills has only appeared in conference abstracts and until the full data are published interpretations are purely speculative.
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The work presented in this chapter has confirmed that jarosite is highly oxidising during pyrolysis experiments and that differences are seen during the heating of different types of jarosite. However, analysis of any jarosite containing sample on Mars will be complicated by the presence of other phases, such as carbonates in windblown sediments. EGA combined with CheMin should give MSL a good understanding of the jarosite in the Pahrump Hills but it is clear that to unlock the full analytical potential of jarosite, including isotope studies, a sample return mission is required.

### 4.12 Conclusions

Martian jarosite provides an environmental indicator of acidic sulfur rich conditions existing at the time of its formation. EGA and XRD may provide further information on the proportion of cations in jarosite, which can inform about the approximate composition of fluids that contributed cations to the jarosite structure. However, the generally potassium rich nature of jarosite, along with sulfur and hydrogen makes it extremely useful for isotopic studies and the full potential of jarosite may only be unlocked when sample return missions become a possibility. In this project, using synthetic jarosite samples, it was conclusively proven that jarosite releases substantial amounts of oxygen during pyrolysis, which poses a significant problem for the detection of high molecular weight organic compounds. The data will prove useful when the full data from the jarosite bearing Pahrump Hills are published. However, this project also demonstrated that studying variations in the jarosite structure using thermal experiments is complicated by the presence of other phases such as carbonates or organic compounds. A rise in carbon dioxide with sulfur dioxide is possible evidence of organic matter oxidation but the presence of carbonates would have to be conclusively ruled out.
Chapter 5 – Perchlorate and jarosite induced combustion of organic matter with variable molecular weights: Implications for identifying indigenous organic matter through Mars missions

The work described in this chapter was published in Geophysical Research Letters.


Chapter 5 is an adaptation and expansion upon this publication and includes additional figures and details of related unpublished experiments.
Mars global image from NASA/JPL-Caltech (2013)
Chapter 5 – Perchlorate and jarosite induced combustion of organic matter

5.1 Introduction

Thermal extraction units were included in the payloads of the Viking and Phoenix Landers and the Mars Science Laboratory (MSL) rover Curiosity (Map 1) but a conclusive detection of indigenous organic matter on Mars remains elusive (Biemann, 1977; Guinn et al., 2008; Mahaffy et al., 2012). The regular delivery of organic matter to the surface of Mars via comets, meteorites and interplanetary dust particles means that some organic matter is expected to be present in martian soils and rocks (Benner et al., 2000; Atreya et al., 2007). Recent results from the Sheepbed mudstone from Yellowknife Bay are possibly indicative of organic matter from a nonterrestrial source (Ming et al., 2014; Grotzinger et al., 2015; Stern et al., 2015).

The lander and rover thermal extraction units, in tandem with sensitive mass spectrometers, were all in good working order (Biemann & Lavoie, 1979; Benner et al., 2000; Ming et al., 2009). The fact the instruments were operating well was demonstrated by atmospheric measurements and the near universal detection of simple organochlorine compounds (Biemann et al., 1977; Leshin et al., 2013; Ming et al., 2014). The organochlorine compounds detected by the Viking instruments were interpreted as terrestrial contamination that was carried to Mars on the landers (Biemann et al., 1977). An alternative theory is that these compounds were in fact the products of reactions between a carbon source and martian perchlorate or other oxychlorines during heating (Navarro-González et al., 2010).

A proportion of the chloromethane and chlorobenzene detected by Curiosity has been interpreted to have possibly formed by reactions between chlorine from martian perchlorate and the leaking derivatization agent N-methyl-N-(tert-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) and 2,6-diphenylphenylene oxide (Tenax) in the hydrocarbon trap (Glavin et al., 2013). During thermal decomposition the perchlorate ion releases chlorine, which can then
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combine with carbon and produce organochlorine compounds (Keller et al., 2006). Chlorine is widespread on the martian surface (Figure 5.1) and perchlorate was detected near the north pole by the Phoenix lander and has been inferred to be present in Gale Crater (Map 3) (Keller et al., 2006; Kounaves et al., 2010; Glavin et al., 2013). However, the hypothesis that chlorination reactions may have occurred in the Viking experiments remains controversial and has been challenged by scientists who worked on the mission (Biemann & Bada, 2011). It is increasingly apparent that much of Mars may host surface materials that will lead to interactions between chlorine and organic matter during thermal experiments.

![Figure 5.1. Global concentrations of chlorine on Mars as measured by Mars Odyssey (Keller et al., 2006).](image)

Perchlorates are known to give off oxygen during thermal decomposition, which can combine with organic matter during thermal experiments to produce carbon dioxide (Devlin & Herley, 1986). The experiments described in Chapters 3 and 4 demonstrated that jarosite also gives off oxygen at temperatures problematic for the detection of organic matter, though at a higher temperatures than perchlorate. Thermal experiments using mixtures containing perchlorate or jarosite could be considered combustion experiments (Devlin & Herley, 1986;
Lewis et al., 2015). Carbon dioxide is frequently detected during thermal experiments on Mars and it is possible a proportion is the result of organic matter oxidation (Leshin et al., 2013; Ming et al., 2014). It is important to consider that in terrestrial samples and potentially martian materials the decarboxylation of organic matter can also produce carbon dioxide unrelated to oxidation (Alencar et al., 1983). In addition the decomposition of carbonates significantly complicates the interpretation of carbon dioxide peaks produced by the heating of complex natural mixtures (Leshin et al., 2013; Lewis et al., 2015).

In previous chapters the negative influence of mineral related oxidation was discussed, principally the resulting weakening and complication of the response for organic matter from heated samples. However, the conversion of organic matter into carbon dioxide can also be a benefit. Carbon dioxide is a simple and easy to handle analyte. In stepped pyrolysis experiments different combustible carbon components can be distinguished at different temperature steps and the resulting peaks for carbon dioxide can inform about the organic content of a sample (Wright & Pillinger, 1989; Sephton et al., 2003). For example, the molecular weight of organic matter in a sample can be indicated from such data. Organic matter of low molecular weight (<500 amu) will combust at lower temperatures relative to high molecular weight organic matter (>1000 amu).

Organic matter in biological materials and in asteroids, comets and interplanetary dust particles predominantly consists of high molecular weight matter. Low molecular weight organic compounds can be highly diagnostic and are amenable to experimentation but are typically a minor component (Killops & Killops, 2005). Any potential organic assemblages on Mars would likely host both low weight and high weight molecular matter. However, the oxidising potential of the martian surface may have removed much of the low weight organic
matter so that martian organic matter is dominated by high molecular weight compounds (Matthewman et al., 2013; Quinn et al., 2013). Indigenous organic matter is almost always characterized by a substantial poorly mobile high molecular weight component while contamination is typically made up of highly mobile low weight organic matter (Sephton et al., 2001; Watson et al., 2003). Distinguishing high molecular weight organic matter from low weight would be useful for interpreting data from Mars. Any sample that was originally organic free and subsequently contaminated, such as by terrestrial contaminants on a rover or lander, would host only low weight organic matter. Despite the negative influences of the chlorination and oxidation reactions caused by perchlorate (Figure 5.2) and jarosite decomposition the transformation of organic matter into organochlorines and carbon dioxide during stepped pyrolysis may still permit discrimination between contamination and indigenous organic matter on Mars. To test this hypothesis organic matter of different molecular weights was heated in the presence of perchlorate and/or jarosite. Prepared low, medium and high molecular weight organic samples were available in the laboratory. The materials supplied were asphaltenes (medium weight) that had been precipitated from an oil sample to leave behind a maltene supernatant (low weight). Maltenes typically have molecular weights <500 atomic mass units (amu) while asphaltenes have molecular weights of approximately 1000 amu. Coal was also provided that had been solvent extracted to leave behind a cross linked organic network of >10,000 amu. Laboratory standards of perchlorate were used and the synthetic potassium jarosite (described in Chapter 4) was selected as it appeared to be more homogeneous than the synthetic sodium jarosite sample. The temperature of release profiles of carbon dioxide from these samples provides guidance on how data from Mars missions can be interpreted and informs on how to discriminate between carbon sources and the influence of different oxidising salts.
Chapter 5 – Perchlorate and jarosite induced combustion of organic matter

5.2 Experimental parameters

5.2.1 Samples

Experiments mimicking those carried out by the 2008 Phoenix Lander suggest that the perchlorate at the landing site was a 60:40 mixture of calcium and magnesium salts (Kounaves et al., 2014). The degradation temperatures of organic matter with distinct molecular weights is likely to remain reasonably similar irrespective of the magnesium to calcium ratio present in perchlorate. In these experiments pure magnesium perchlorate (Mg(ClO₄)₂) sourced from Fisher Scientific was mixed with the three organic matter types. The perchlorate was originally anhydrous but as it is a hygroscopic material it became rapidly hydrated once exposed to the atmosphere. Working in a fume hood reduced the rate at which the perchlorate hydrated and made sample loading easier as the hydrated form was somewhat adhesive.

Jarosite on Mars exists somewhere between the potassium, sodium and hydronium endmembers (Klingelhofer et al., 2004). The synthetic potassium jarosite sample was used in
this work as during the stepped pyrolysis experiments discussed in Chapter 4 it produced less variation between repeat experiments than the sodium jarosite, suggesting it was more homogeneous. It is also the most thermodynamically stable form of jarosite (Dutrizac & Jambor, 2000).

The methods that had been used to prepare the laboratory standards of organic matter used in this project are described in the following paragraph. The oil that provided the low and medium weight organic fractions was sourced from Osmington Mills, Dorset, United Kingdom (Figure 5.3). At this locality the Lower Jurassic Blue Lias marine shales host type II kerogens before migration and exposure at the surface. The asphaltenes were precipitated from the sample using an excess of n-hexane with a twelve hour settling time followed by centrifugation, the process was repeated three times. Following precipitation the supernatants were collected and combined for the low weight maltene fraction. The coal sample was taken from the seven foot seam in Taff Merthyr, South Wales. The high molecular weight fraction of the coal was isolated by extracting the material with 93:7 dichloromethane: methanol solvent mixture and repeating the extraction three times.

The organic materials and salt mixtures were combined at a mass ratio of 1:1 and 1:1:1 (when the coal was mixed with both jarosite and perchlorate). Jarosite was only mixed with the coal as the relatively high decomposition temperature of jarosite means that interaction with low and medium weight organic matter would be minimal. Selecting a mixing ratio was complicated by the estimation of the indigenous organic carbon content of martian samples. Perchlorate on Mars is likely present at low levels as at the Phoenix landing site perchlorate salts made up 0.6% of the leachable soil mass (Hecht et al., 2009). Any organic matter on Mars is probably at very low levels so a mixing ratio of 1:1 was assumed to be a reasonable and
practical assumption. Deducing the exact ratio is not crucial as the aim was to identify the
major reaction products and the temperatures of their release.

![Image](image.jpg)

Figure 5.3. The oil that supplied the maltenes and asphaltenes for this project was sourced from the sandstones in the cliffs of Osmington Mills, seen here during a postgraduate field trip in 2013.

The magnesium perchlorate and potassium jarosite were added to the pyrolysis tubes as powders. The maltenes and asphaltenes were dissolved in dichloromethane and syringed on to the perchlorate in the pyrolysis tubes. These samples were allowed to dry for 72 hours to ensure that no residual dichloromethane remained in the tube. For the coal experiments the powdered material was gradually added to the tubes containing perchlorate and/or jarosite until a 1:1 (or 1:1:1) ratio was attained.
5.2.2 Pyrolysis-gas chromatography-mass spectrometry (py-GC-MS)

The experiments were conducted using the CDS 5200 pyroprobe connected to the Agilent Technologies 6890 gas chromatograph coupled to the 5973 spectrometer described in Chapter 2. During pyrolysis samples were run at 100 °C steps between 200 °C and 800 °C. The GC injector was held at 200 °C and operated in split mode (35:1) with separation performed on a J&W GS-Q PLOT column. The GC oven was held for five minutes at 35 °C and then ramped at a rate of 10 °C min\(^{-1}\) to 200 °C where it was held for four minutes. Mass spectra were acquired in the range 10-150 amu. Data are presented in a semiquantitative form by normalizing peak area against perchlorate or jarosite mass in milligrams.
5.3 The thermal decomposition of organic matter with variable molecular weights mixed with oxidising salts

5.3.1 Pure perchlorate decomposition products

To properly assess the products of reactions between organic matter and perchlorate the magnesium perchlorate powder was first heated in isolation so that the type and relative abundance of species contributed by the mineral could be identified (Figure 5.4).

Figure 5.4. The species detected during stepped pyrolysis of magnesium perchlorate, peak areas are normalised against perchlorate mass (in milligrams).
Molecular oxygen was first detected at 400 °C and produced a sharp peak at 600 °C. At higher temperatures oxygen production rapidly declined. Water production was relatively high at the starting temperature of 200 °C but fell sharply and was around background levels from 500 °C and above. The hydration of the magnesium perchlorate powder during sample preparation is the inferred source of this water. Carbon dioxide was first detected at 400 °C and was produced at low levels other than a very slight rise from 600 °C. A minor carbonate impurity was possibly responsible for the high temperature peak but the detection of minor carbon tetrachloride and carbon monoxide suggests there was also some minor organic matter contamination that was oxidised and chlorinated during heating. Simple organochlorines such as chloromethane, dichloromethane or phosgene were not detected. Hydrochloric acid produced a similar temperature profile to oxygen indicating it was also generated by the thermal decomposition of magnesium perchlorate. Water and chlorine can combine to form hydrochloric acid, which explains its production in this experiment (Treger & Rozanov, 1989).

The decomposition products of synthetic potassium jarosite have already been well characterised in Chapter 4. Synthetic potassium jarosite shows a water peak at 450 °C, sulfur dioxide evolution starting at 500 °C and peaking at 700 °C, with oxygen showing a very similar profile to sulfur dioxide, carbon dioxide was detected at all temperatures but at very low amounts suggesting very minor organic contamination.
5.3.2 Perchlorate and maltenes (low molecular weight) decomposition products

Several of the volatile species that were produced during the thermal decomposition of a 1:1 mixture of maltenes and magnesium perchlorate show substantially different temperature profiles relative to their production from the pure perchlorate standard (Figure 5.5).

![Graph showing the thermal decomposition products of a 1:1 mixture of magnesium perchlorate and maltenes.](image)

Figure 5.5. The products of the thermal decomposition of a 1:1 mixture of magnesium perchlorate and maltenes, peak areas are normalised to the mass of perchlorate in milligrams.
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Oxygen production shows two peaks, one at 400 °C and another at 600 °C. The higher temperature peak is similar to that seen in the perchlorate-only experiment but somewhat smaller. At 400 °C there are also sharp peaks for carbon dioxide, carbon monoxide and smaller broader peaks for hydrochloric acid, phosgene and carbon tetrachloride, the same temperature step as the lower-temperature oxygen peak. All of these species, other than phosgene, were detected in the perchlorate only experiment but their peaks were either significantly smaller or showed a substantially different temperature profile. Therefore, it can be stated that these compounds show evidence of an interaction between perchlorate and organic compounds, which led to the formation of chlorinated compounds and an increased production of carbon dioxide and carbon monoxide. Phosgene can be synthesised by reactions between carbon monoxide and chlorine in the presence of a carbon catalyst, which may explain its detection in this experiment (Schneider & Diller, 2000).

Above 500 °C the chromatograms appear very similar to those seen in the perchlorate only experiment. Oxides of carbon are at a low abundance, oxygen shows a large peak at 600 °C and hydrochloric acid shows a moderate peak. This suggests that below 500 °C the perchlorate was interacting with the decomposing organic matter while at greater temperatures the organic matter was exhausted and the remaining perchlorate decomposed as normal. Water was the only species not to show a substantial difference from perchlorate-only decomposition at any temperature, which suggests water production is primarily related to the decomposition of the hydrated perchlorate.
5.3.3 Perchlorate and asphaltenes (medium molecular weight) decomposition products

The thermal decomposition products of a 1:1 mixture of asphaltenes and magnesium perchlorate show different temperature profiles to both the maltenes mixture and perchlorate on its own (Figure 5.6).

Figure 5.6. The products of the thermal decomposition of a 1:1 mixture of magnesium perchlorate and asphaltenes, peak areas are normalised to the mass of perchlorate in milligrams.
The difference between this mixture and the maltenes mixture indicates that the nature of the organic matter that is interacting with perchlorate exerts an influence on the temperature profiles of the resulting volatiles.

Oxygen shows a single sharp peak at 500 °C, higher than the 400 °C peak seen in the maltenes experiment but lower than the 600°C peak produced by pure perchlorate. Hydrochloric acid, carbon tetrachloride and phosgene also peak at 500 °C, which supports the hypothesis that their production is related to the interactions between decomposing organic matter and perchlorate.

Carbon dioxide production forms a very broad peak with peak production at 400 °C, this is the same temperature for peak production as for the maltenes mixture but the peak is much greater and does not decline significantly until 600 °C. Carbon monoxide also produced a broad peak with peak production at 500 °C. Water production is again similar to that seen in the perchlorate-only experiment suggesting that water loss from the hydrated mineral was the major source of water released during thermal decomposition.
5.3.4 Perchlorate and coal (high molecular weight) decomposition products

The products of the thermal decomposition of a 1:1 mixture of magnesium perchlorate and coal show temperature profiles that are distinct from the other experiments other than for oxygen and water (Figure 5.7).

![Graph showing the products of thermal decomposition](image)

**Figure 5.7.** The products of the thermal decomposition of a 1:1 mixture of magnesium perchlorate and coal, peak areas are normalised to the mass of perchlorate in milligrams.
Chapter 5 – Perchlorate and jarosite induced combustion of organic matter

Water shows a temperature profiles similar to those seen in the mineral-only experiment indicating the hydrated perchlorate was the major source of water production. Oxygen peaks sharply at 600 °C, the same as pure perchlorate indicating that in contrast with the maltenes or asphaltenes responses the decomposition temperature of perchlorate is not affected by the presence of coal.

However, coal does show an influence over the production of other compounds during the thermal decomposition of the mixture. Carbon dioxide shows a very broad hump that begins at 300 °C and does not return to low levels until 700 °C. Unlike the other experiments carbon monoxide does not peak at the same temperature as the oxygen peak with a very broad but small peak appearing with the first detection of oxygen at 400 °C.

Hydrochloric acid, phosgene and carbon tetrachloride all peak at 600 °C along with oxygen. Not surprisingly these experiments demonstrate that there appears to be a relationship between peak perchlorate decomposition and peak chlorinated compound production. The broad carbon dioxide peak indicates that there are a complex series of decomposition and reaction steps occurring with increasing temperature. At 400 °C chlorination is minor but carbon dioxide production is major suggesting some oxidation and decarboxylation of the coal is occurring. Chlorine does not begin to interact significantly with organic matter until 600 °C.
5.3.5 Jarosite and coal (high molecular weight) decomposition products

If potassium jarosite is mixed with coal at a 1:1 ratio rather than perchlorate several changes in the temperature profiles of different volatiles can be observed (Figure 5.8).

Figure 5.8. The products of the thermal decomposition of a 1:1 mixture of potassium jarosite and coal, peak areas are normalised to the mass of jarosite in milligrams.
The atomic oxygen released during the thermal decomposition of jarosite appears to be completely consumed by oxidising reactions. No oxygen was detected at any temperature step despite the substantial sulfur dioxide production observed from 500 °C. The initial high water values seen in the previous figures are absent indicating that perchlorate was contributing this water. The moderate temperature water peak related to dehydroxylation of jarosite is present, along with the slight rise at higher temperature related to hydration of the potassium sulfate intermediate formed during jarosite thermal decomposition.

Carbon dioxide is produced with a sharp high temperature peak indicating that the oxidising influence of jarosite is focused at 600 °C while perchlorate is problematic at lower temperatures. Carbon monoxide rises with carbon dioxide and shows a slight peak at 600 °C coinciding with the first large increase in sulfur dioxide.

The absence of perchlorate meant that no chlorination reactions occurred and several decomposition products of the coal were observed that differed from those seen when mixed with perchlorate. Ethane and propane production is likely related to the carbon tetrachloride detected in the other experiments. Benzene and toluene were also produced. The interaction between atomic oxygen from jarosite and organic matter appears to often lead to the production of benzene, as it has been observed in many of the experiments described in Chapters 3 and 4.
5.3.6 Perchlorate, jarosite and coal (high molecular weight) decomposition products

When jarosite is added to a mixture of magnesium perchlorate and coal at a ratio of 1:1:1 there are several observations that demonstrate that both the salts were interacting with organic matter during thermal decomposition (Figure 5.9).

![Diagram showing peak areas of various decomposition products normalized to the combined mass of salt in milligrams.]

Figure 5.9. The products of the thermal decomposition of a 1:1:1 mixture of magnesium perchlorate, potassium jarosite and coal, peak areas are normalised to the combined mass of salt in milligrams.
Chapter 5 – Perchlorate and jarosite induced combustion of organic matter

Water showed a broad low temperature peak that demonstrates the combination of dehydration via the loss of hydroxyl groups from the jarosite structure on top of the previously observed dehydration of perchlorate. An increase in water production was seen at 800 °C, which is related to hydration and dehydration of the potassium sulfate formed as an intermediate in potassium jarosite decomposition, as discussed fully in Chapter 4.

Sulfur dioxide produced a large peak with the first detection made at 500 °C rising to a broad peak from 600 to 700 °C. Decomposition of the sulfate ions within jarosite leading to sulfur dioxide release began 50 °C lower and peaked 100 °C lower than during thermal decomposition of the pure synthetic standard. The temperature profile for oxygen appears extremely similar to that produced by pure perchlorate and the coal and perchlorate mixture. The oxygen produced by jarosite must have been consumed in oxidising reactions as it was when jarosite and coal were mixed (Figure 5.8). The carbon dioxide and carbon monoxide temperature profiles show broad peaks with an increase in carbon dioxide production at 800 °C indicating that jarosite extends the oxidation range to higher temperatures.

The peaks for hydrochloric acid and carbon tetrachloride are smaller than in the perchlorate and coal mixture. The presence of atomic oxygen and increased carbon monoxide in the reaction chamber may have led to greater production of phosgene. Chlorobenzene was also detected, which was absent in the heating products of the perchlorate and coal mixture further indicating that jarosite exerts an influence on the pyrolysis products. The benzene and toluene observed in the coal and jarosite mixture were chlorinated when mixed with perchlorate.
5.4 Carbon dioxide and molecular weight information

The variation in carbon dioxide production seen with organic matter with different molecular weights indicates that such data can indicate the presence of organic matter and give an indication of the type of material present (Figure 5.10).

![Graphs showing carbon dioxide production from perchlorate and organic matter of different molecular weights.](image)

Figure 5.10. Carbon dioxide production from 1:1 mixtures of perchlorate and (a) low weight organic matter and (b) medium weight organic matter, (c) shows the production of carbon dioxide from high molecular weight organic matter and perchlorate and jarosite, peak areas are normalised to salt mass.
Stepped combustion of organic matter containing samples in order to discriminate contamination from indigenous carbonaceous components has been long practiced but using other oxidation methods rather than the oxidising reactions caused by the presence of perchlorate and jarosite (Swart et al., 1983). For oxygen sourced from perchlorate decomposition, the coevolution of chlorinated hydrocarbons provides additional evidence of thermally sensitive organic material. The evidence for oxidation resulting from jarosite is less obvious, atomic oxygen appears to be readily consumed in the reaction vessel and difficult or impossible to detect. It will be important to consider on Mars if jarosite or other ferric sulfates are present as an amorphous component in materials as a mixture of perchlorate and jarosite produced a different organochlorine assemblage than when perchlorate was mixed with coal on its own. The detection of low weight organic matter only (evidenced by a low temperature sharp carbon dioxide peak) would require consideration that terrestrial contamination may have been delivered on the spacecraft and further blanks and controls would be needed to assess the likelihood of this further. If contamination is ruled out then an alternative explanation would have to be considered. A subsurface hydrocarbon seep could result in a concentration of more mobile low molecular weight in the near surface. Models suggest that high molecular weight organic compounds are more susceptible to alteration by radiation relative to light weight organic compounds (Pavlov et al., 2012), which may lead to the accumulation of light organic compounds in irradiated surface deposits. If only high molecular weight organic matter was inferred to be present it would suggest a sample that had been processed and oxidised. If a mix of both low and high molecular weights is inferred it would suggest the sample hosts a complex suite of organic matter originating either from biological or nonbiological processes on Mars or from meteorites.
5.5 Implications and discussion

When comparing data from this project and that returned by Mars Science Laboratory (MSL) from Mars it is important to consider that the experiments were operating under different conditions. However, the two techniques share enough common features that comparisons between the data are still relevant (Table 5.1).

<table>
<thead>
<tr>
<th>Instrument</th>
<th>MSL [Glavin et al., 2013]</th>
<th>This study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature programme</td>
<td>30°C (0 min), 35 °C/min, 835°C (0 min)</td>
<td>30°C (0 min), 20 °C/mS, 200 °C to 800 °C (0.25 min)</td>
</tr>
<tr>
<td>He pressure (mbar)</td>
<td>25</td>
<td>492</td>
</tr>
<tr>
<td>He flow rate (ml/min)</td>
<td>0.8</td>
<td>57</td>
</tr>
<tr>
<td>Split ratio</td>
<td>800:1</td>
<td>50:1</td>
</tr>
<tr>
<td>Transfer line (°C)</td>
<td>135</td>
<td>150</td>
</tr>
<tr>
<td>Traps</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Hydrocarbon trap</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Cryofocus</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Gas chromatograph</td>
<td>MXT-CLP</td>
<td>J&amp;W GS-Q PLOT</td>
</tr>
<tr>
<td>He flow rate (ml/min)</td>
<td>0.4</td>
<td>2</td>
</tr>
<tr>
<td>Split ratio</td>
<td>250:1</td>
<td>35:1</td>
</tr>
<tr>
<td>50°C (4 min), 10 °C/min, 220 °C (3 min)</td>
<td>35°C (0 min), 10 °C/min, 200 °C (4 min)</td>
<td></td>
</tr>
<tr>
<td>Mass spectrometer</td>
<td>2-535</td>
<td>10-150</td>
</tr>
</tbody>
</table>

5.5.1 Water

Evolved gas analyses (EGA) of the Rocknest aeolian materials and the Cumberland and John Klein mudstone samples produced low-temperature water that declined with increasing temperature. Multiple sources were suggested including water adsorbed onto the powders, structural water in salts, phyllosilicates and iron oxyhydroxides (Leshin et al., 2013; Ming et al., 2014). It was also suggested that some of the water detected from the Sheepbed mudstone may have been as a result of the oxidation of organic matter (Ming et al., 2014).

The data from the perchlorate containing samples analysed in this project show a similar temperature of release profile for water to that seen in MSL data. The addition of different
forms of organic matter did not create any major variations in water production indicating that the water detected was overwhelmingly derived from the hydrated perchlorate. When jarosite was present in the mixture a higher temperature peak around 400-500 °C was detected. Perchlorate and jarosite could account for some of the low and moderate temperature water production on Mars.

5.5.2 Oxides of carbon

In the Sheepbed mudstone experiments, particularly Cumberland, a peak in carbon dioxide was associated with the onset of hydrochloric acid generation (Ming et al., 2014), which led to the suggestion that acid dissolution of carbonates may produce carbon dioxide. In this project carbon dioxide was seen to correlate with hydrochloric acid in carbonate free samples so the correlation between the gases may not be highly diagnostic of acid dissolution during EGA.

Carbon dioxide peak release temperatures in the Rocknest materials (Leshin et al., 2013) were around 100 °C higher than those seen in the Sheepbed samples (Ming et al., 2014), with the higher temperature peak representing carbonate decrepitation and the lower temperature peak reflecting possible organic matter combustion. The carbon dioxide profiles seen in Figure 5.10 clearly show that variation in the molecular weight of organic matter can also generate differences in peak release temperatures.

If organic matter was the sole source of the carbon dioxide peaks in the Rocknest and Sheepbed materials then the sharp and relatively low temperature of release seen in the Sheepbed mudstone would suggest low molecular weight organic matter. The broader and higher temperature peak seen in Rocknest would suggest moderate weight organic matter. Iron sulfates were also inferred to be possibly present in the Rocknest material and absent in
the Sheepbed mudstone (Leshin et al., 2013). In Figure 5.9 the presence of jarosite was seen to cause a broader production of carbon dioxide but the carbon dioxide peak is seen at around 350 °C -400 °C in Rocknest, which is too low for jarosite to be a cause. A lot of uncertainty exists over assuming the carbon dioxide production in the Sample Analysis at Mars (SAM) experiments is purely from organic matter, particularly regarding the presence of carbonates, assessing the production of chlorinated organic compounds needs to be considered before organic matter can be identified as a probably source of the MSL carbon dioxide.

5.5.3 Organochlorine compounds

The temperature profiles produced by the different mixtures analysed in these experiments reveal a correlation between organochlorine compounds and carbon dioxide that may be diagnostic. The EGA of the Rocknest materials showed a release of organochlorine compounds with a maximum at 250 °C (Leshin et al., 2013). However, the carbon dioxide detected in Rocknest peaked around 400 °C (Leshin et al., 2013). The absence of a correlation of peak-release temperature for carbon dioxide and organochlorine compounds differs from the patterns seen in the results presented in this chapter and suggests the carbon dioxide detected in Rocknest was from a nonorganic source.

Analysis of the materials from the John Klein and Cumberland drill sites showed that carbon dioxide and organochlorine compound production peaked together at approximately 250 °C (Ming et al., 2014). Such a low temperature of release (with a relatively sharp carbon dioxide peak) appears similar to the results seen for the pyrolysis of a mixture of perchlorate and low weight organic matter. This contributes further evidence in favour of the hypothesis that the Sheepbed mudstone sample contained organic matter (Grotzinger et al., 2015).
Chapter 5 – Perchlorate and jarosite induced combustion of organic matter

5.5.4 Oxygen

Oxygen evolution initiated at a lower temperature in the Sheepbed mudstone samples (Ming et al., 2014) compared to the Rocknest aeolian samples (Leshin et al., 2013). A lower temperature release for oxygen was seen when perchlorate was mixed with low weight organic matter. The double peak seen in the John Klein sample (Ming et al., 2014) is remarkably similar to the double peak seen in the perchlorate and maltenes mixture. This observation also suggests the presence of a low molecular weight organic component present in the Sheepbed mudstone.

5.5.5 Confidence Hills

The Confidence Hills data are discussed separately as not all of the data have been published at the time of writing and only the trends for water, carbon dioxide, oxygen and sulfur dioxide are currently available. Water production at Confidence Hills shows a similar trend to Rocknest, with a broad low to moderate temperature peak and low levels at high temperatures (Leshin et al., 2013; Franz et al., 2015). Jarosite is known to be present at Confidence Hills (Rampe et al., 2015), and perchlorate is also likely contributing some of the water observed. Carbon dioxide peaks are observed at approximately 150 °C and 400 °C, with a broad shoulder up to 500 °C and a small broad peak at 800 °C (Franz et al., 2015). Multiple peaks suggest multiple sources of carbon are present in Confidence Hills. The 150 °C carbon dioxide peak has been suggested to be the release of adsorbed carbon dioxide (McAdam et al., 2015). The shoulder up to 500 °C correlates with a peak in oxygen (hydrochloric acid and organochlorines were reported but not the temperature of release has not yet been published) (McAdam et al., 2015). Low molecular weight organic matter does not appear to be present in the Confidence Hills sample as the relatively high oxygen peak is similar to that
seen at Rocknest and dissimilar to the results of the perchlorate and maltenes experiment. The peak in sulfur dioxide at 800 °C is coupled with peaks in carbon dioxide and molecular oxygen (Franz et al., 2015; McAdam et al., 2015). Jarosite is present at trace amounts so an amorphous component in Confidence Hills is suggested as a possible source of the high temperature sulfur dioxide (McAdam et al., 2015). Oxygen from the sulfur dioxide ion fragmenting on the mass spectrometer explains the oxygen peak seen at 600 °C but not all of the peak at 800 °C (Franz et al., 2015; McAdam et al., 2015). If the oxygen detected at this temperature is sourced from sulfate decomposition it suggests that little to no organic matter was decomposing at 800 °C as there was no substantial sink for oxygen, though the carbon dioxide peak at the same temperature suggests some organic matter have been completely oxidised until carbon was exhausted.

5.5.6 Synthesis

Insights from the stepped heating of oxidising salts and organic matter of variable molecular weights suggest that the existing data from EGA data from Rocknest shows a carbon dioxide source that is inorganic while the Sheepbed mudstone samples contains a carbon dioxide source that is organic. The temperatures of release and the correlation with organochlorine compounds seen in the Sheepbed samples suggests the presence of low molecular weight organic matter, which would be consistent with either contamination or migrated or radiolytically processed indigenous organic matter.
5.6 Conclusions

Perchlorate-induced combustion interferes with organic analyses on Mars. Jarosite induced combustion would also interfere with the detection of high molecular weight organic matter. Perchlorate is a more aggressive oxidant but jarosite extends oxidation processes to higher temperatures. Despite this the carbon dioxide resulting from organic matter oxidation can still be used to reveal the nature of organic matter present in a sample. Stepped heating reveals that carbon dioxide and chlorinated organic compounds can be produced at the same temperature step to reveal the occurrence of organic matter and its molecular weight. An understanding of molecular weight is important as it can be used to discriminate between contamination and indigenous organic matter. Low molecular weight material only would suggest contamination while high molecular weight would suggest indigenous carbon.
Chapter 6 – The geological preservation of a sulfate-rich ecosystem
Mars global image from NASA/JPL-Caltech (2013)
6.1 Introduction

The experimental work discussed in previous chapters involved the use of individual natural or synthetic samples. While the results of these projects have demonstrated and quantified the complicating influence of jarosite on organic molecule detection, the continuous mineralogical and organic compound variation across a single natural jarosite forming system has not yet been studied in detail. The collection of multiple samples from a naturally varying environment would be more closely relevant to the sampling opportunities offered during a Mars mission.

The acidic stream discovered in St. Oswald’s Bay, named as Pequeño Río Tinto (PRT), was first sampled in 2012 and provided the sample PRT that was used in the quantitative study described in Chapter 4. In 2013 further sampling was carried out at the stream and a series of cores were taken across a four metre study area (see Figure 6.1, sampling is discussed fully in Chapter 2). Layers within each core were then identified and separated. This sampling allowed both the horizontal and vertical variation across the system to be investigated. The experiments in this project are designed to be broadly analogous to the operations of a Mars rover where samples are extracted and powdered and then heated. However, while missions such as Mars Science Laboratory (MSL) primarily use evolved gas analysis (EGA), our experiment use pyrolysis-gas chromatography-mass spectrometry (py-GC-MS), though the two methods are very similar (a more detailed comparison is made in the previous chapter).

The presence of biological materials such as grass, wood, moss and a microbial mat allows the potential inputs of organic matter into the system to be assessed. Investigating how the mineralogy interacts with these compounds will provide an insight into how martian jarosite forming systems could have potentially preserved organic matter.
The jarosite outcrops observed on Mars are generally inferred to have formed by surface/near-surface aqueous alteration over short time scales and possibly at low temperatures (Milliken et al., 2008; Berger et al., 2009). Investigating the mineralogy of the sulfate ecosystem present at PRT provides further information on the mineral assemblages produced by localised surface releases of sulfate rich acidic waters. The chromatograms for the pyrolysis products of each layer can be related to the results of inorganic phase quantification by X-ray diffraction (XRD) and the minerals that are optimal targets for organic compound exploration on Mars in sulfate-rich regions can be identified. Jarosite has already been inferred to potentially preserve organic matter (Aubrey et al., 2006; Kotler et al., 2009). The ability of pyrolysis-GC-MS techniques to detect this potential organic matter can be thoroughly tested with the sulfate ecosystem materials.
Measurements and observations made during core extraction allowed the aqueous and redox chemistry of the sulfate ecosystem to be estimated. The small stream was highly acidic, with a pH of 3.5. In Figure 6.1 the grey-yellow sandy-clay seen to the left of the stream was found to be hard and dry when dug into and jarosite appeared as a common surface phase. To the right of the stream the majority of the study area had a surface dominated by iron oxides and a microbial mat. When the cores were cut from this part of the study area the holes quickly filled up with water (Figure 6.2). Jarosite containing layers were found immediately under the iron oxide crusts with jarosite concentration appearing to decrease with depth. When core 5 was extracted there was a strong smell of hydrogen sulfide suggesting the waterlogged sandy-clay becomes reducing at a relatively shallow depth. The jarosite and iron oxide forming region appeared to occur only down to a depth of around 10 cm.
Jarosite is only stable at a pH below 3 and in less acidic conditions it eventually breaks down to the iron oxide mineral goethite (Figure 6.3) (Stoffregen et al., 2000).

\[
\text{KFe}_2\text{(SO}_4\text{)}_2\text{(OH)}_6(s) \leftrightarrow 3 \text{FeO(OH)}(\text{goethite}) + K^+(\text{aq}) + 2 \text{SO}_4^{2-}(\text{aq}) + 3 H^+(\text{aq})
\]

Figure 6.3. The decomposition of jarosite into goethite (Stoffregen et al., 2000)

The near surface weathered zone (gossan) of iron and sulfur containing ore bodies is often goethite rich and jarosite poor with jarosite only being abundant at depth (Dutrizac & Jambor, 2000). The sulfate ecosystem shows a similar behaviour on a much smaller scale. At the surface direct contact with the atmosphere and precipitation, in addition to the waterlogged soils seen to the right of the stream (Figure 6.1), would decompose jarosite rapidly while at a few centimetres depth the slower rate of oxidation and saturation with acidic waters allows jarosite to persist for longer. The fact that the sandy-clay to the left of the stream (Figure 6.1) is dry means the decomposition reactions at this locality are probably much slower and enable jarosite’s persistence at the surface.

6.2 Experimental parameters

Pyrolysis-GC-MS

Ten mg of each powdered sample was pyrolysed at 650 °C. A solvent delay of 2.5 minutes was added to the GC-MS method file to prevent excessive amounts of sulfur dioxide damaging the mass spectrometer. The gas chromatograph injector was held at 270 °C and operated in split mode (10:1) with a column flow rate of 1.1 mL min\(^{-1}\). Separation was performed on a J&W DB-5MS UI column (30 m x 0.25 mm x 0.25 µm). The gas chromatograph oven was held for 2 min at 40 °C and then ramped to 310 °C where it was held for 10 minutes. Mass spectra were acquired in the scan range 45-550 amu. A full method description is given in Chapter 2.
X-ray diffraction

After dividing the cores into layers there were 27 mineral samples to analyse. An autosampler coupled to a Philips PW 1830 enabled rapid analysis of the large number of samples. The quantitative results are presented alongside the chromatograms for each mineral layer.
6.3 Analysis of cores

6.3.1 Core 1

The samples taken from core 1 were a sandy-clay and grass that capped the core (Figure 6.4).

A photo of the study area is shown in Figure 6.5.

![Figure 6.4. Chromatograms showing the pyrolysis products of the grass and sandy-clay found in core 1. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence, ane indicates an alkane and ene indicates an alkene.]
### Table 6.1. Pyrolysis products identified in 1G: Grass

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 3-methyl</td>
<td>8</td>
<td>Phenol, 2-methoxy-4-methyl</td>
<td>15</td>
<td>Octadecanoic acid</td>
</tr>
<tr>
<td>2</td>
<td>Acetic acid</td>
<td>9</td>
<td>Phenol, 4-ethyl-2-methoxy</td>
<td>16</td>
<td>Eicosanoic acid</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>10</td>
<td>Phenol, 2,6-dimethoxy</td>
<td>17</td>
<td>Cyclotetracosane</td>
</tr>
<tr>
<td>4</td>
<td>Furfural</td>
<td>11</td>
<td>Phenol, 2-methoxy-5-(1-propenyl)-(E)-</td>
<td>18</td>
<td>Stigmastan-3,5-diene</td>
</tr>
<tr>
<td>5</td>
<td>Styrene</td>
<td>12</td>
<td>Dodecanoic acid</td>
<td>19</td>
<td>Stigmastan-3,5-dien-7-one</td>
</tr>
<tr>
<td>6</td>
<td>2-Furancarboxaldehyde, 5-methyl</td>
<td>13</td>
<td>Hexadecanoic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Phenol, 3-methyl</td>
<td>14</td>
<td>Oleic acid</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 6.2. Pyrolysis products of 1C: Sandy-clay

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 3-methyl</td>
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<tr>
<td>2</td>
<td>Benzene</td>
</tr>
<tr>
<td>3</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
</tr>
<tr>
<td>5</td>
<td>Furfural</td>
</tr>
<tr>
<td>6</td>
<td>Phenol</td>
</tr>
</tbody>
</table>
Figure 6.5. Core 1 immediately after extraction showing the sandy-clay with a cap of grass.
Chapter 6 – The geological preservation of a sulfate rich ecosystem

Mineralogy

The grass capping core 1 was growing in a substrate rich in quartz and clay minerals with trace amounts of the feldspar mineral microcline. The influence of the acidic sulfate-rich waters from the nearby stream appears to be low as only 1% jarosite was detected.

Organic chemistry

The focus of this work is on mineralogy and how it captures and preserves organic matter within the sulfate ecosystem and if pyrolysis is a suitable analytical method for such materials. A single pyrolysis analysis of the biological materials found within each core was deemed satisfactory to give a broad overview of the inputs of organic matter into the study area. It is also similar to the whole-sample analyses performed by the Viking landers and Mars Science Laboratory. The types of organic matter detected through pyrolysis of the grass include plant sterols, fatty acids, alkanes and alkenes, toluene, styrene acetic acid, heterocyclic compounds such as furan and furfural and phenyl compounds with various functional groups. The exact carbon number of the alkanes and alkenes could not be assigned with confidence due to the complex and noisy signal resulting from the natural sample. The sandy-clay the grass was growing in did not record the organic chemistry of the grass well. Pyrolysis of the sandy-clay detected only furan, furfural, benzene, toluene, acetic acid and phenol. Clays are often target minerals for organic matter detection missions as organic matter and phyllosilicates are hydrodynamic equivalents (Sephton, 2010). In the sulfate ecosystem organic matter is being formed and deposited on pre-existing clays and in this scenario organic matter preservation in the clay minerals appears to be poor.
6.3.2 Core 2

The samples taken from core 2 were a sandy-clay with some wood fragments (Figure 6.6). A photo of the study area is shown in Figure 6.7.

Figure 6.6. Chromatograms showing the pyrolysis products of the wood and sandy-clay found in core 2. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence, ane indicates an alkane and ene indicates an alkene, S indicates siloxanes – material from the chromatography column.
### Table 6.3. Pyrolysis products identified in 2W: Wood

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 2-methyl-</td>
<td>12</td>
<td>Phenol, 2-methoxy</td>
<td>24</td>
<td>Ethanone, 1-(3-hydroxy-4-methoxyphenyl)</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
<td>13</td>
<td>Phenol, 4-methyl</td>
<td>25</td>
<td>Phenol, 2-methoxy-4-propyl</td>
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<td>Acetic acid</td>
<td>14</td>
<td>Phenol, 2,4-dimethyl</td>
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<td>Beta-D-glucopyranose, 1,6-anhydro-</td>
</tr>
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<td>4</td>
<td>1H-Pyrrole, 1-methyl-</td>
<td>15</td>
<td>Phenol, 4-ethyl</td>
<td>27</td>
<td>Phenol, 2,6-dimethoxy-4-(2-propenyl)-</td>
</tr>
<tr>
<td>5</td>
<td>Toluene</td>
<td>16</td>
<td>Phenol, 2-methoxy-4-methyl</td>
<td>27*</td>
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<td>6</td>
<td>Furfural</td>
<td>17</td>
<td>Phenol, 4-ethyl-2-methoxy</td>
<td>28</td>
<td>Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)</td>
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<tr>
<td>6*</td>
<td>Furfural*</td>
<td>18</td>
<td>2-methoxy-4-vinylphenol</td>
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<td>E-9-Tetradecanoic acid</td>
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<td>7</td>
<td>Benzene, 1,3,-dimethyl</td>
<td>19</td>
<td>1,2-Benzenediol,4-methyl</td>
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<td>9,12-Octadecadienoic acid (Z,Z)</td>
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<td>8</td>
<td>Styrene</td>
<td>20</td>
<td>Phenol, 2-methoxy-3-(2-propenyl)</td>
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<td>Stigmasta-3,5-dien-7-one</td>
</tr>
<tr>
<td>9</td>
<td>2-Furancarboxaldehyde,</td>
<td>21</td>
<td>Phenol, 2-methoxy-4-(1-propenyl)</td>
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<tr>
<td>10</td>
<td>Phenol</td>
<td>22</td>
<td>Vanillin</td>
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<tr>
<td>11</td>
<td>Phenol, 2-methyl</td>
<td>23</td>
<td>Phenol, 2-methoxy-4-(1-propenyl)</td>
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<td></td>
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</table>

*Peaks that give an identical match suggesting only minor differences in the functional groups.

### Table 6.4. Pyrolysis products of 2C: Sandy-clay

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
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<tbody>
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<td>Pyridine</td>
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<td>6</td>
<td>Furfural</td>
</tr>
<tr>
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<td>Acetic acid</td>
<td>7</td>
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</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>8</td>
<td>Styrene</td>
</tr>
</tbody>
</table>
Figure 6.7. The cut made to extract core 2 is seen close to the edge of the sulfate ecosystem at the boundary between sandy-clay dominated sections and sulfur and iron mineral dominated sections.
Chapter 6 – The geological preservation of a sulfate rich ecosystem

*Mineralogy*

The mineralogy of core 2 is broadly similar to that seen in core 1 as the substrate is rich in quartz and clay minerals. However, at this locality jarosite makes up 8% of the core rather than 1%, which indicates the greater influence that acidic waters exert on mineralogy as sampling moved closer to the acidic stream. No iron oxide was detected indicating that the jarosite is either stable, in an environment where jarosite only breaks down very slowly, or that the iron oxide is X-ray amorphous or at very low abundance.

*Organic chemistry*

Lignin is a major component of wood and during wood pyrolysis phenols are released via the cleavage of ether and carbon-carbon linkages (Mohan *et al*., 2006). This explains the large number of phenol compounds detected during pyrolysis of the wood found in core 2. As with the core 1 grass, compounds such as furan, furfural, alkanes, alkenes, toluene, styrene and a plant sterol were also detected. Fatty acids were present but with a smaller number of species compared to pyrolysis of grass. The detection of a sugar, beta-d-glucopyranose, indicates that the material is fresh as the sugar has not yet been completely metabolised by microbes. Nitrogen containing compounds in the wood and sandy-clay suggest the presence of proteins (Kaal *et al*., 2009). The sandy-clay collected at core 2 gives a similar response to core 1 during pyrolysis but 8 species were detected rather than 6. Despite the solvent delay, some sulfur dioxide was detected due to the large amount produced by the greater concentration of jarosite. Acetic acid, benzene, furfural and toluene were detected, as they were in core 1. The detection of additional pyridine, ethylbenzene and styrene perhaps reflects the greater input of phenyl compounds from the wood in the core as well as proteins.
6.3.3 Core 3

The samples taken from core 3 were a microbial mat capping iron oxide over a sandy-clay (Figure 6.8). A photo of the study area is shown in Figure 6.9.

Figure 6.8. Chromatograms showing the pyrolysis products of the microbial mat, rusty crust and sandy-clay found in core 3. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence, ane indicates an alkane and ene indicates an alkene, S indicates siloxanes – material from the chromatography column.
Table 6.5. Pyrolysis products identified in 3M: Microbial mat

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 2-methyl-</td>
<td>8</td>
<td>Ethanone, 1-(2-Furanyl)</td>
<td>14</td>
<td>Napthalene</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
<td>9</td>
<td>2-Furancarboxaldehyde, 5-methyl-</td>
<td>15</td>
<td>1,4:3,6-Dianhydro-alpha-d-glucopyranose</td>
</tr>
<tr>
<td>3</td>
<td>Furan, 2,5-dimethyl-</td>
<td>9*</td>
<td>2-Furancarboxaldehyde, 5-methyl-</td>
<td>16</td>
<td>beta-D-glucopyranose, 1,6-anhydro</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>10</td>
<td>Benzonitrile</td>
<td>17</td>
<td>Hexadecanoic acid</td>
</tr>
<tr>
<td>5</td>
<td>3-Furaldehyde</td>
<td>11</td>
<td>Phenol, 4-methyl</td>
<td>18</td>
<td>Oleic acid</td>
</tr>
<tr>
<td>6</td>
<td>Furfural</td>
<td>12</td>
<td>Maltol</td>
<td>19</td>
<td>Octadecanoic acid</td>
</tr>
<tr>
<td>7</td>
<td>Styrene</td>
<td>13</td>
<td>Benzy nitrile</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Peaks that give an identical match suggesting only minor differences in the functional groups.

Table 6.6. Pyrolysis products of 3R: Rusty crust

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzene</td>
</tr>
<tr>
<td>2</td>
<td>Thiophene</td>
</tr>
<tr>
<td>3</td>
<td>Sulfur dioxide</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
</tr>
<tr>
<td>5</td>
<td>Thiophene, 3-methyl</td>
</tr>
</tbody>
</table>

Table 6.7. Pyrolysis products of 3C: Sandy-clay

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulfur dioxide</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
</tr>
</tbody>
</table>
Chapter 6 – The geological preservation of a sulfate rich ecosystem

Mineralogy

The top layer of core 3 hosted a fibrous microbial mat and was quartz rich with major goethite and jarosite. The iron oxide layer beneath the mat contained 72% goethite with lesser quartz and jarosite. The base of the core was more similar to the sandy-clays seen in cores 1 and 2 but illite was absent and kaolinite made up only 4% of the core.

Figure 6.9. The hole cut to extract core 3. The distinct layering of fibrous microbial mat over a thin rusty layer and then a jarosite containing sandy-clay can be clearly seen. Examples of the fragments of wood that can be observed throughout much of the study area can be seen in the top right and the bottom of the image.
Organic matter

From the locations of cores 3 to 5, the sampling areas were typically covered by a fibrous purple mat with a distinctive surface sheen that was inferred to be a microbial mat. The microbes in this environment must be acid-resistant organisms that are involved in sulfur oxidation and/or reduction. Two sugar molecules were detected during pyrolysis of the microbial mat layer indicating the material sampled in this core was fresh. Fatty acids were also detected along with a small number of alkanes and an alkene. Benzene, toluene, fufural, styrene, phenyl and furan compounds were also detected. A detection of benzonitrile provided evidence for proteins (Kaal et al., 2009). The species detected in the mineral layers underneath the mat were again poorly representative of the biological materials in close proximity. Sulfur dioxide and benzene were detected in both the rusty crust and the sandy-clay. However, the rusty crust also produced toluene, thiophene and methylthiophene during pyrolysis. Thiophene and methylthiophene are evidence of an interaction between sulfur and organic matter. It is inferred that this was an indigenous process occurring in PRT and not during pyrolysis. Jarosite (and therefore sulfur) is present in the majority of samples analysed but thiophenes are only detected in layers in which a substantial amount of goethite exists. Low temperature natural vulcanisation that forms intermolecular sulfur linkages between organic compounds has been inferred to occur in early diagenesis (Ruble & Philp, 1995). Thiophenes are products of laboratory analogues to such natural vulcanisation reactions (Kowalewski et al., 2010). When jarosite decomposes into goethite sulfate is released (Figure 6.3), sulfur-reducing bacteria may utilise this sulfate and the reduced sulfur is then incorporated into organic matter. This is also a possible explanation for the smell of hydrogen sulfide during extraction of core 5, where reduced sulfur combines directly with hydrogen.
6.3.4 Core 4

The samples taken from core 4 were a microbial mat capping iron oxide over a sandy-clay (Figure 6.10). A photo of the study area is shown in Figure 6.11.

Figure 6.10. Chromatograms showing the pyrolysis products of the microbial mat, rusty crust and sandy-clay found in core 4. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence and ene indicates an alkene.
Table 6.8. Pyrolysis products identified in 4M: Microbial mat

<table>
<thead>
<tr>
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<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 2-methyl-</td>
<td>12</td>
<td>Acetophenone</td>
<td>23</td>
<td>Benzonitrile, 2-methyl-</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
<td>13</td>
<td>Benzonitrile, 4-methyl</td>
<td>24</td>
<td>Napthalene, 2-methyl-</td>
</tr>
<tr>
<td>3</td>
<td>Pyridine</td>
<td>14</td>
<td>Benzo[1,2-]furans, 2-methyl</td>
<td>25</td>
<td>Biphenyl</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>15</td>
<td>Benzyl nitrile</td>
<td>26</td>
<td>Cyclotetradecane</td>
</tr>
<tr>
<td>5</td>
<td>3-Furaldehyde</td>
<td>16</td>
<td>Benzene, pentyl-</td>
<td>27</td>
<td>Thiophene, 3-phenyl-</td>
</tr>
<tr>
<td>6</td>
<td>Furfural</td>
<td>17</td>
<td>Napthalene</td>
<td>28</td>
<td>Pyridine, 2-phenyl-</td>
</tr>
<tr>
<td>7</td>
<td>Styrene</td>
<td>18</td>
<td>2-Benzothiophene</td>
<td>29</td>
<td>Dibenzofuran</td>
</tr>
<tr>
<td>8</td>
<td>Ethane, 1-(2-furanyl)-</td>
<td>19</td>
<td>Isoquinoline</td>
<td>30</td>
<td>Fluorene</td>
</tr>
<tr>
<td>9</td>
<td>2-Furancarboxaldehyde, 5-methyl-</td>
<td>20</td>
<td>1H-Inden-1-one, 2,3-dihydro-</td>
<td>31</td>
<td>Dibenzothiophene</td>
</tr>
<tr>
<td>10</td>
<td>Benzonitrile</td>
<td>21</td>
<td>1-Tridecane</td>
<td>32</td>
<td>Pentadecanenitrile</td>
</tr>
<tr>
<td>11</td>
<td>Phenol</td>
<td>22</td>
<td>Napthalene, 1-methyl-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.9. Pyrolysis products identified in 4R: Rusty crust

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 2-methyl-</td>
<td>6</td>
<td>Styrene</td>
<td>11</td>
<td>Napthalene, 2-ethenyl</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
<td>7</td>
<td>Benzonitrile</td>
<td>12</td>
<td>Dibenzofuran</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>8</td>
<td>Indene</td>
<td>13</td>
<td>Fluorene</td>
</tr>
<tr>
<td>4</td>
<td>Thiophene, 3-methyl-</td>
<td>9</td>
<td>Napthalene</td>
<td>14</td>
<td>Dibenzothiophene</td>
</tr>
<tr>
<td>5</td>
<td>Ethylbenzene</td>
<td>10</td>
<td>Benzo[b] thiophene</td>
<td>15</td>
<td>Phenanthrene</td>
</tr>
</tbody>
</table>

Table 6.10. Pyrolysis products of 4C: Sandy-clay

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulfur dioxide</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
</tr>
</tbody>
</table>
Unlike in core 3 the upper layers of core 4 did not host jarosite. Only goethite and quartz were the major components in both the microbial mat and the rusty crust layers. The base of the core was made up of a quartz-rich layer with 7% jarosite and minor kaolinite and microcline. The lack of jarosite suggests that there has been a complete decomposition to goethite in the upper layers. This would indicate that the upper layers sampled in core 4 are either older than those sampled in core 3 or were being decomposed more rapidly.

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Organic matter

No sugars were detected during pyrolysis of the microbial mat found at the top of the core. This suggests the organic matter in core 4 is more degraded relative to core 3. Some peaks detected in core 3 were not possible to identify due to the large number of masses recorded by the mass spectrometer. In core 4 the majority of peaks can be identified. Several thiophene compounds were detected, which along with the lack of sugars suggests that decomposition and vulcanisation of organic matter has occurred at the top of core 4. Several compounds containing nitrogen were detected and phenyl groups were abundant.

The rusty crust underneath the microbial mat was found to produce thiophenes and phenyl groups as well as alkenes during pyrolysis. Core 4 was poorly consolidated and there is a risk that some of the microbial mat may have been intermixed with the rusty crust. However, variations in quartz and iron oxide abundance would be unlikely to exert a significant influence on the products of pyrolysis so the differences seen are related to differences in organic matter content. The sandy-clay underlying the rusty crust and microbial mat gave a very poor response for organic matter as only a small peak for benzene was observed. The near surface mineralisation observed so far suggests a sulfate ecosystem deposits a very thin mineral layer and the organic molecules associated with such a system also appear to be constrained to these layers.
6.3.5 Core 5

The samples taken from core 5 were wood fragments and an iron oxide crust over a sandy-clay (Figure 6.12). A photo of the study area is shown in Figure 6.13.

Figure 6.12. Chromatograms showing the pyrolysis products of the wood, rusty crust and sandy-clay found in core 5. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence, ane indicates an alkane and ene indicates an alkene, $S$ indicates siloxanes – material from the chromatography column.
### Table 6.11. Pyrolysis products identified in 5W: Wood

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 2-methyl</td>
<td>11</td>
<td>Phenol, 2-methoxy</td>
<td>21</td>
<td>Phenol, 2-methoxy-4-(1-propenyl)</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
<td>12</td>
<td>Phenol, 2,4-dimethyl</td>
<td>22</td>
<td>Ethanone, 1-(4-hydroxy-3-methoxyphenyl)</td>
</tr>
<tr>
<td>3</td>
<td>Furan, 2,5-dimethyl</td>
<td>13</td>
<td>Phenol, 2-methoxy-4-methyl</td>
<td>23</td>
<td>Benzoic acid, 4-hydroxy-3-methoxy, methyl ester</td>
</tr>
<tr>
<td>4</td>
<td>Acetic acid</td>
<td>14</td>
<td>3,4-Dimethoxytoluene</td>
<td>24</td>
<td>Phenol, 2,6-dimethoxy-4-(2-propenyl)</td>
</tr>
<tr>
<td>5</td>
<td>Toluene</td>
<td>15</td>
<td>Phenol, 4-ethyl-2-methoxy</td>
<td>25</td>
<td>3-Hydroxy-4-methoxybenzoic acid</td>
</tr>
<tr>
<td>6</td>
<td>Furfural</td>
<td>16</td>
<td>1,2-Benzenediol, 3-methoxy</td>
<td>26</td>
<td>Phenol, 2,6-dimethoxy-4-(2-propenyl)-</td>
</tr>
<tr>
<td>7</td>
<td>Styrene</td>
<td>17</td>
<td>2-methoxy-4-vinylphenol</td>
<td>27</td>
<td>Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-</td>
</tr>
<tr>
<td>8</td>
<td>2-Furancarboxaldehyde, 5-methyl</td>
<td>18</td>
<td>Phenol, 2,6-dimethoxy</td>
<td>28</td>
<td>Benzoic acid, 4-hydroxy-3,5-dimethoxy-,hydrazide</td>
</tr>
<tr>
<td>9</td>
<td>Phenol</td>
<td>19</td>
<td>Vanillin</td>
<td>29</td>
<td>Hexadecanoic acid</td>
</tr>
<tr>
<td>10</td>
<td>Phenol, 2-methyl</td>
<td>20</td>
<td>Benzoaldehyde, 3-hydroxy-4-methoxy</td>
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<td></td>
</tr>
</tbody>
</table>

### Table 6.12. Pyrolysis products identified in 5R: Rusty crust

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 3-methyl</td>
<td>5</td>
<td>Furfural</td>
<td>9</td>
<td>Napthalene</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
<td>6</td>
<td>Bicyclo[4.2.0]octa-1,3,5-triene</td>
<td>10</td>
<td>Benzo[1] thiophene</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>7</td>
<td>Benzoaldehyde</td>
<td>11</td>
<td>Dibenzothiophene</td>
</tr>
<tr>
<td>4</td>
<td>Thiophene, 3-methyl</td>
<td>8</td>
<td>Benzonitrile</td>
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</tr>
</tbody>
</table>

### Table 6.13. Pyrolysis products identified in 5CT: Sandy-clay (upper)

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 3-methyl</td>
<td>3</td>
<td>Toluene</td>
<td>5</td>
<td>Benzenes, 1,2,3-trimethyl</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
<td>4</td>
<td>p-Xylene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.13. Core 5 was cut just to the side of one of the small streams that ran over this part of the study area. Like the main stream the water was full of green particulates and highly acidic.
Mineralogy

The microbial mat and rusty crust could not be separated in core 5 so they were sampled as one layer. The crust had a similar mineralogy to that seen in core 4. Jarosite was absent and quartz and goethite were the major phases. The smell of hydrogen sulfide during extraction of the core indicated that the subsurface was partially reducing but no reduced minerals were detected during XRD of the layers. The quartz-rich layer immediately under the rusty crust contained 20% clay but towards the base only quartz with minor amounts of microcline were detected.

Organic chemistry

The wood discovered within core 5 did not produce sugars or plant sterols during pyrolysis suggesting it was somewhat more degraded than the wood discovered in core 2. Many different phenyl compounds, a fatty acid and benzene, toluene, furan and furfural were observed. The species discovered in the core 5 rusty crust were not as diverse as those seen in the same mineralogy in core 4 but again this layer appeared to be the optimal mineral layer for organic compound preservation within the core mineralogy. Thiophenes were detected along with naphthalene and toluene, and benzene. The clay immediately underneath the rusty crust contained a furan, benzene, toluene and other benzene rings with methyl groups. The base of the core, where conditions may have been reducing yielded only benzene during pyrolysis. The activity of sulfur-reducing bacteria related to the liberation of sulfate when jarosite decomposes to goethite is a plausible alternative hypothesis for the smell of hydrogen sulfide.
6.3.6 Core 6

The samples taken from core 6 were a moss and rust cap covering a quartz sand nodule over a jarosite rich quartz-sand (Figure 6.14). A photo of the study area is shown in Figure 6.15.

![Figure 6.14. Chromatograms showing the pyrolysis products of the nodule exterior and interior and sandy-clay found in core 6. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence and S indicates siloxanes – material from the chromatography column.](image-url)
### Table 6.14. Pyrolysis products identified in 6E: Exterior of nodule

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 2-methyl</td>
<td>7</td>
<td>Styrene</td>
<td>13</td>
<td>Benzyl nitrile</td>
</tr>
<tr>
<td>2</td>
<td>Sulfur dioxide</td>
<td>8</td>
<td>Furan, 2-ethyl-5-methyl</td>
<td>14</td>
<td>Napthalene</td>
</tr>
<tr>
<td>3</td>
<td>Acetic acid</td>
<td>9</td>
<td>2-Furancarboxaldehyde, 5-methyl</td>
<td>15</td>
<td>Benzo[b]thiophene</td>
</tr>
<tr>
<td>4</td>
<td>Pyridine</td>
<td>10</td>
<td>Benzonitrile</td>
<td>16</td>
<td>Napthalene, 2-ethenyl-</td>
</tr>
<tr>
<td>5</td>
<td>Thiophene, 3-methyl</td>
<td>11</td>
<td>Phenol</td>
<td>17</td>
<td>Dibenzothiophene</td>
</tr>
<tr>
<td>6</td>
<td>Furfural</td>
<td>12</td>
<td>Phenol, 4-methyl</td>
<td>18</td>
<td>Hexadecanenitrile</td>
</tr>
</tbody>
</table>

### Table 6.15. Pyrolysis products of 6C: Sandy-clay

<table>
<thead>
<tr>
<th>No.</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulfur dioxide</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
</tr>
</tbody>
</table>
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Figure 6.15. The section cut before extraction of core 6 is seen in the centre of the photo, the largest stream that passes through the study area is immediately to the left.
Mineralogy

The layering seen in core 6 was quite distinct from that seen in the previous 5 cores described so far. The top of the core consisted of a rounded homogenous looking sandy nodule capped with a thin layer of iron oxide, jarosite and moss. Separating the very thin layers that made up the cap was not possible so they were sampled as one layer named as the exterior of the nodule. The mineralogy of the cap included quartz, goethite, clays and minor jarosite and microcline. The core of the nodule was almost entirely quartz with a trace amount of sanidine. The core was extracted at a high point next to the stream that may have formed by a slump of sandy material onto the study area. The slight elevation may have made the environment slightly less acidic allowing the moss to grow. The base of the core was a quartz sand with 26% jarosite.

Organic chemistry

The compounds detected during pyrolysis of the core exterior were similar to those detected during pyrolysis of the rusty crusts and microbial mat present in other cores. Thiophenes, nitrogen containing compounds and naphthalene were detected. The core of the nodule did not contain any organic matter detectable by pyrolysis, which is unsurprising considering it was almost entirely quartz. The base of the core, with its high jarosite content, produced sulfur dioxide, benzene and toluene during pyrolysis. The observations so far suggest that jarosite does contain some organic matter but accessing it through pyrolysis is challenging, typically only sulfur dioxide and very simple compounds can be detected. The observations from cores 3-6 suggest that goethite formed from the decomposition of jarosite may also host organic matter.
6.3.7 Core 7

The samples taken from core 7 were a wood fragment, whole core powder and a sample from a lighter-coloured sublayer (Figure 6.16). A photo of the study area is shown in Figure 6.17.

Figure 6.16. Chromatograms showing the pyrolysis products of the microbial mat, rusty crust and sandy-clay found in core 7. All chromatograms are presented at the same scale. S indicates siloxanes – material from the chromatography column.
### Table 6.16. Pyrolysis products of 7W: Wood

<table>
<thead>
<tr>
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<tbody>
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<tr>
<td>2</td>
<td>Benzene</td>
</tr>
<tr>
<td>3</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
</tr>
<tr>
<td>5</td>
<td>Furfural</td>
</tr>
<tr>
<td>6</td>
<td>Styrene</td>
</tr>
<tr>
<td>7</td>
<td>Benzonitrile</td>
</tr>
</tbody>
</table>

### Table 6.17. Pyrolysis products of 7C

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</thead>
<tbody>
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</tr>
<tr>
<td>2</td>
<td>Benzene</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
</tr>
<tr>
<td>4</td>
<td>Benzonitrile</td>
</tr>
</tbody>
</table>

### Table 6.18. Pyrolysis products of 7J

<table>
<thead>
<tr>
<th>No.</th>
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</tr>
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<tbody>
<tr>
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<td>Sulfur dioxide</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
</tr>
</tbody>
</table>
Mineralogy

Though layering was observed in the walls of the hole cut to extract core 7 and the core itself the thin layers were extremely difficult to separate during division of the core. A section of
the core that appeared lighter in colour was separated out but XRD of both the whole core powder and this lighter layer produced essentially the same result, a quartz sand with major jarosite and 8-9% kaolinite. Iron oxide was not detected suggesting the layering was either related to clays or a very thin band of iron oxide that was either amorphous or not sufficiently abundant in the powders to be detected. As goethite has been seen to possibly preserve organic matter in the previous cores examined these possible iron oxide layers would be of major interest for any future field work carried out by other researchers in the area.

*Organic chemistry*

The wood fragment found within core 7 gave a very poor response for organic compounds during pyrolysis relative to the wood fragments found in cores 2 and 5. Only weak peaks for benzene, toluene, furfural, styrene and benzonitrile were detected. This indicates that this wood fragment was highly degraded and likely much older than the materials found on the other side of the stream. Pyrolysis of the whole core powder produced benzene, toluene, benzonitrile and sulfur dioxide. The light coloured sublayer produced only sulfur dioxide and benzene. Before pyrolysis core 7 had been considered to be one of the most promising samples collected from the study area as the observed layering may have indicated the preservation of repeated deposits of jarosite and partial decomposition to goethite. Instead the waterlogged units on the other side of the stream that were rich in goethite gave the best response for organic matter. This suggests that when analysing the geological remains of a sulfate ecosystem considering the lateral placement of the sampling points is of critical importance.
6.3.8 Core 8

The samples taken from core 8 were sandy-clays and a jarosite nodule (Figure 6.18). A photo of the study area is shown in Figure 6.19.

Figure 6.18. Chromatograms showing the pyrolysis products of the materials found in core 8. All chromatograms are presented at the same scale. S indicates siloxanes – material from the chromatography column.
Table 6.19. Pyrolysis products of 8CT

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzene</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
</tr>
</tbody>
</table>

Table 6.20. Pyrolysis products of 8W

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 3-methyl-</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
</tr>
</tbody>
</table>

Table 6.21. Pyrolysis products of 8WJ

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 3-methyl-</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
</tr>
</tbody>
</table>

Table 6.22. Pyrolysis products of 8J

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzene</td>
</tr>
<tr>
<td>2</td>
<td>Sulfur dioxide</td>
</tr>
</tbody>
</table>

Table 6.23. Pyrolysis products of 8CB

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulfur dioxide</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
</tr>
</tbody>
</table>
Figure 6.19. The hole dug to extract core 8 is seen towards the bottom of the photo. Unlike core 7, which partially filled with water (though not to the extent of that seen in cores 2-6) after digging the core 8 hole remained dry.
Mineralogy

When core 8 was cut in half a wood-like layer was seen halfway down that when cut open hosted a jarosite nodule. Analysis of the sandy-clay throughout the core and the wood layer showed a mineralogy similar to that seen in core 1. The materials were quartz rich with major phases of kaolinite and illite and minor jarosite and microcline. The jarosite nodule contained 41% sodium jarosite and appeared chemically distinct from the other jarosites sampled so far, which matched with more potassium rich forms.

Organic chemistry

As with core 7, the response for organic matter from all layers within the core was poor. The layer that was interpreted as wood differed only from the surrounding clay by the production of methylfuran during pyrolysis. The clay above the wood produced only benzene and toluene while the jarosite nodule and the clay beneath the wood produced benzene and sulfur dioxide. Any material containing 41% jarosite would be an extremely difficult sample to analyse for organic matter through pyrolysis due to the substantial production of oxygen. As with observations of the other sandy-clay samples it appears that clay minerals and organic matter need to be deposited together for substantial preservation to occur. In a situation like the sulfate ecosystem, where organic compounds would be added to the surface of a pre-existing mass of clay minerals, preservation appears to be poor.
6.3.9 Core 9

The sample taken from core 9 was a sandy-clay (Figure 6.20). A photo of the study area is shown in Figure 6.21.

![Figure 6.20. Chromatograms showing the pyrolysis products of the microbial mat, rusty crust and sandy-clay found in core 9. All chromatograms are presented at the same scale. S indicates siloxanes – material from the chromatography column.](image)

**Table 6.24. Pyrolysis products of 9C**

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzene</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
</tr>
</tbody>
</table>

Mineralogy

The mineralogy of core 9 was similar to that seen in core 1. The core was quartz rich with 10% clays and minor jarosite and microcline.

Organic chemistry

The only compounds detected during pyrolysis of the material collected from core 9 were benzene and toluene.
Figure 6.21. Core 9 is in the foreground of this photo shot across the study area. The sharp contrast between the environments on each side of the stream that runs between cores 6 and 7 can be seen. In the foreground the surface and near subsurface is dry and sandy with jarosite increasingly common at the surface closer to the stream. In the background beyond the stream the surface and subsurface are waterlogged and covered mostly with a rusty crust capped with a microbial mat.
6.3.10 Wood fragments and mineral crusts near core 8

During the extraction of cores 8 and 9 it was noticed that a fragment of wood embedded in the quartz sand had many yellow crystals growing on and around it. In the field these crystals were interpreted as jarosite and were sampled along with the wood to investigate whether the minerals were preserving any of the organic matter of the wood they were growing on (Figure 6.22). A photo of the study area is shown in Figure 6.23.

![Chromatograms showing the pyrolysis products of the wood fragments and mineral crusts found near core 8. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence, ene indicates an alkene and S indicates siloxanes – material from the chromatography column.](image-url)
### Table 6.25. Pyrolysis products identified in W

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 2-methyl</td>
<td>8</td>
<td>Phenol</td>
<td>15</td>
<td>Phenol, 4-ethyl-2-methoxy</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
<td>9</td>
<td>Phenol, 2-methyl</td>
<td>16</td>
<td>2-methoxy-4-vinylphenol</td>
</tr>
<tr>
<td>3</td>
<td>Acetic acid</td>
<td>10</td>
<td>Phenol, 4-methyl</td>
<td>17</td>
<td>Phenol, 2,6-dimethoxy</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>11</td>
<td>Benzofuran, 2-methyl</td>
<td>18</td>
<td>4-hydroxy-2-methoxybenzaldehyde</td>
</tr>
<tr>
<td>5</td>
<td>Furfural</td>
<td>12</td>
<td>Phenol, 2,4-dimethyl</td>
<td>19</td>
<td>Phenol, 2-methoxy-3-(2-propenyl)</td>
</tr>
<tr>
<td>6</td>
<td>Styrene</td>
<td>13</td>
<td>Phenol, 2-methoxy-4-methyl</td>
<td>20</td>
<td>Ethanone, 1-(4-hydroxy-3-methoxyphenyl)</td>
</tr>
<tr>
<td>7</td>
<td>2-Furancarboxaldehyde, 5-methyl</td>
<td>14</td>
<td>1,2-Benzenediol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 6.26. Pyrolysis products of JW

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulfur dioxide</td>
</tr>
<tr>
<td>2</td>
<td>Trichloromethane</td>
</tr>
<tr>
<td>3</td>
<td>Carbon tetrachloride</td>
</tr>
<tr>
<td>4</td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>5</td>
<td>Benzene, 1,3,4-trichloro</td>
</tr>
<tr>
<td>6</td>
<td>Benzene, 1,2,3,4-tetrachloro</td>
</tr>
<tr>
<td>7</td>
<td>Benzene, 1,2,3,5-tetrachloro-</td>
</tr>
<tr>
<td>8</td>
<td>Benzene, pentachloro</td>
</tr>
</tbody>
</table>
Mineralogy

The interpretation made in the field, that the yellow crystals found on the wood fragments near core 8 were predominantly jarosite, was found to be incorrect after XRD analysis of the powdered crystals. The major phase was a mineral called metasideronatrite (Na₂Fe(SO₄)₂(OH)(H₂O)), which has a similar chemical structure to jarosite. Quartz was also present, along with gypsum, sodium jarosite and halite. Discussions with workers at the
Natural History Museum revealed that a sodium-rich mineralogy is typical of minerals formed by sea spray. The identification of halite (at an abundance of 2%) was uncertain but was confirmed by scanning electron microscopy.

Organic chemistry

Pyrolysis of the wood gave a relatively poor response for organic matter similar to that seen in the wood fragments found in cores 7 and 8. This suggests that the organic matter on this side of the stream is largely degraded. Only a few strong peaks for phenyl group compounds and furfural and methyl furan were seen. Pyrolysis of the mineral crusts produced predominantly chlorinated organic matter, the only sample from the study area to do so. Halite is the only mineral present in the powder known for certain to contain chlorine, however its high decomposition temperature means that the organochlorines would have to have been present in situ and not formed during pyrolysis. The fact that these crystal formed by sea spray and that seawater has abundant aqueous chlorine makes an in situ formation a plausible explanation. However, seawater typically contains both organochlorines and organobromines (Abrahamsson & Ekdahl, 1996; Sim et al., 2009), and the latter were not conclusively detected in this material. Chlorine substitution for the hydroxyl groups within metasideronatritle or sodium jarosite is another hypothesis. Such a process was considered as during phase quantification of the mineral powder the Rietveld refinement would only fit well if the unit cell of the reference pattern for metasideronatritle was adjusted slightly suggesting some minor compositional difference between the database reference pattern and the metasideronatritle collected in St. Oswald’s Bay. This is investigated further in Section 6.5.
6.3.11 Stair Hole core

The samples taken from Stair Hole were a dried-out microbial mat and jarosite and rust rich layers (Figure 6.24). A photo of the study area is shown in Figure 6.25.

![Chromatograms](image)

**Figure 6.24.** Chromatograms showing the pyrolysis products of the microbial mat, jarosite and rust layers found at Stair Hole. All chromatograms are presented at the same scale. ? denotes a peak that cannot be identified with confidence and S indicates siloxanes – material from the chromatography column.
### Table 6.27. Pyrolysis products identified in SHM: Stair Hole microbial mat

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furan, 2-methyl</td>
<td>8</td>
<td>Styrene</td>
<td>15</td>
<td>Benzo [b] thiophene</td>
</tr>
<tr>
<td>2</td>
<td>Acetic acid</td>
<td>9</td>
<td>2-Furancarboxaldehyde, 5-methyl</td>
<td>16</td>
<td>Benzenepropenonitrile</td>
</tr>
<tr>
<td>3</td>
<td>Pyridine</td>
<td>10</td>
<td>Benzonitrile</td>
<td>17</td>
<td>Napthalene, 2-ethenyl</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>11</td>
<td>Phenol</td>
<td>18</td>
<td>Pentadecane</td>
</tr>
<tr>
<td>5</td>
<td>Furfural</td>
<td>12</td>
<td>Phenol, 4-methyl</td>
<td>19</td>
<td>Pentadecanenitrile</td>
</tr>
<tr>
<td>6</td>
<td>Ethylbenzene</td>
<td>13</td>
<td>Benzonitrile, 2-methyl</td>
<td>20</td>
<td>n-hexadecanoic acid</td>
</tr>
<tr>
<td>7</td>
<td>o-Xylene</td>
<td>14</td>
<td>Napthalene</td>
<td>21</td>
<td>9-Octadecenoic acid (Z), methyl ester</td>
</tr>
</tbody>
</table>

### Table 6.28. Pyrolysis products of SHJT

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
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</thead>
<tbody>
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<td>1</td>
<td>Sulfur dioxide</td>
</tr>
<tr>
<td>*</td>
<td>Tentative thiophene</td>
</tr>
</tbody>
</table>

### Table 6.29. Pyrolysis products of SHR

<table>
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<tr>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulfur dioxide</td>
</tr>
<tr>
<td>2</td>
<td>Thiophene</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
</tr>
</tbody>
</table>

### Table 6.30. Pyrolysis products of SHJB

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulfur dioxide</td>
</tr>
<tr>
<td>*</td>
<td>Tentative thiophene</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
</tr>
<tr>
<td>3</td>
<td>Thiophene, 3-methyl</td>
</tr>
</tbody>
</table>
Figure 6.25. The microbial mat preserved at Stair Hole appeared desiccated however when the core was remove the base of the hole developed a small layer of water. The small stream to the left of the photo was found to have a pH of 5.
Chapter 6 – The geological preservation of a sulfate rich ecosystem

**Mineralogy**

The mineralogy of the top layer was quartz, clay and goethite rich with 6% jarosite. At depth the clays were absent and jarosite was concentrated in an upper layer and a lower layer at 12-19% abundance. Goethite was most concentrated in a rusty crust found in the middle of the core but there was a general trend of goethite concentration increasing with depth.

**Organic chemistry**

The pyrolysis products of the desiccated microbial mat found at Stair Hole are similar to those seen produced by the pyrolysis of cores 3 and 4. Pentadecanenitrile was observed in core 4 and carboxylic acids in core 3. Benzene, toluene, furfural, furan and phenyl groups were also detected. The stream at Stair Hole appears relatively inactive relative to PRT and the materials and organic matter in this system are more degraded. It can still be clearly seen that the Stair Hole core was dug in the centre of a system similar to that at PRT. Thus the mineral layers here are somewhat older and their organic compound preservation after a longer time period relative to PRT can be assessed. The upper jarosite-rich layer produced only a tentative detection for thiophene. Thiophene was evidenced by the detection of an m/z 84 peak on the mass spectrometer. The rusty crust in the middle of the core produced a clear peak for thiophene and toluene. The lower jarosite-rich layer produced a tentative detection for thiophene, toluene and methyl-thiophene.

The clearest detection of thiophene was made when goethite concentration was highest and jarosite concentration was lowest. Other projects described in this thesis have proven that jarosite is destructive and disruptive to organic matter during pyrolysis experiments and this is one factor that would cause thiophene detection to vary. Another potential contribution is
that the most goethite-rich layer was likely the layer that has experienced the most aqueous alteration. A sustained supply of water would be beneficial to organisms and the rusty crust may be preserving a time when the system was most habitable to life.

6.4 Unit cell parameters of jarosite crystals across the PRT and Stair Hole study sites

When jarosite is present in a powder at 5% abundance or above then profile fitting during phase quantification using XRD and Rietveld refinement can be used to infer the potassium, sodium and hydronium ratio of the jarosite phase (Figure 6.26) (Basciano & Peterson, 2008).

![Figure 6.26. The unit cell of every jarosite phase found in the study areas at 5% abundance or greater is plotted on the axes of Basciano and Peterson (2008). The unit cell parameters a and c allows the potassium, sodium and hydronium abundances to be estimated. PRT indicates the composition of the jarosite collected in the study area in 2012.](image)

The majority of the phases analysed show that jarosite forming at PRT and Stair Hole is predominantly potassium rich with minor sodium and hydronium. Two outliers are seen, JW and 8J. JW is sodium jarosite with no potassium and minor hydronium, the mineral crust it originated from is inferred to have formed from sea spray. 8J is an intermediate between sodium and potassium with minor hydronium. 8J was found in what has been interpreted as a highly degraded layer of wood. At the surface close to the location from which core 8 was
taken was the sodium rich mineralised crust growing on wood (of which the sodium rich jarosite of JW was a component). It is inferred that 8J is a buried equivalent of JW. Over time it was likely altered by potassium-rich fluids from the present day sulfate stream (the jarosite from core 7, from which 7C and 7J were collected, was potassium rich). These details show that using XRD analysis to estimate the unit cell of jarosite can be a useful tool for investigating the origin of mineral layers and the cation content of fluids. The potassium jarosite rich sample collected from the sulfate ecosystem site in 2012 (PRT in Figure 6.26) is seen to have a slightly different composition from the majority of materials sampled a year later. PRT was sampled close to where cores 2 and 3 were removed in 2013, the jarosite sampled in 2012 appears to have originated from a more potassium depleted fluid.

6.5 Scanning electron microscopy (SEM) analysis of wood fragments and mineral crust

The mineral encrusted wood found near core 8 produced organochlorines during pyrolysis. The wood itself appeared degraded but produced a suite of organic molecules without chlorine. As the minerals are interpreted to be the result of sea spray and seawater can contain organochlorines this result is not entirely unexpected. However, the major mineral phase in the crust was metasideronatrite and it could only be quantified when the Rietveld refinement fit was allowed to adjust the reference unit cell for metasideronatrite suggesting some sort of compositional difference between the reference and the material collected at St. Oswald’s Bay. Sodium jarosite was also present but during refinement to quantify the phases it fit well with the reference pattern. Both metasideronatrite and sodium jarosite have hydroxyl groups that could potentially be substituted for chlorine. Scanning electron microscopy was carried out (method described fully in Chapter 2) to examine the element chemistry of the mineral crusts and wood, the observations are shown in Figures 6.27-6.30.
Figure 6.27. SEM image of an example of a wood fragment with a mineral crust. The elemental composition of each scan area is shown below the image.
Figure 6.28. SEM image of the area studied by scans 2 and 5 in Figure 6.27. The elemental composition of each scan area is shown below the image.
Figure 6.29. SEM image of the area studied by scan 3 in Figure 6.27. The elemental composition of each scan area is shown below the image.
Figure 6.30. SEM image of the JW powder. The elemental composition of each scan area is shown below the image.
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The observations from SEM analysis indicate that chlorine is found on both mineral and wood surfaces. This suggests that a marine origin for the organochlorine compounds is the most probable hypothesis. In Figure 6.27 spectra 1, 3 and 4 show indistinct peaks for chlorine on the mineral crust, while spectrum shows elevated levels of chlorine at the wood-mineral boundary and spectrum 5 indicates the presence of halite crystals. Figure 6.28 shows how the wood surface, far from any obvious major crystals, has high levels of chlorine suggesting a veneer of organochlorines. When the whole wood sample was pyrolysed the low abundance of organochlorines would be difficult or impossible to distinguish from the unchlorinated organic matter that makes up most of the wood. However, in the mineral crusts these organochlorines would be concentrated, which explains their detection. Aluminium is frequently detected and substitution of this element for iron in metasideronatrite could explain why the unit cell of the JW material differed from that described in the XRD database. Figure 6.29 shows evidence for quartz and gypsum, which aided the XRD investigations. Figure 6.30 reveals the angular crystals that make up the JW powder, bromine was detected in spectrum 1 as well as chlorine indicating that further pyrolysis of the powder could potentially produce organobromines as well as organochlorines. In the other spectra peaks for sulfur, iron, oxygen and sodium are again coupled with aluminium, which suggests that an Fe: Al ratio difference in the St. Oswald’s Bay metasideronatrite could explain the difference from the reference pattern.

6.6 An overview of the sulfate ecosystem

A simplified diagram of the mineral layers of the sulfate ecosystem and the organic matter contained within them is presented in Figure 6.31.
Figure 6.31: The mineralogy and organic molecule content of the sulfate-rich ecosystem. Though core dimensions and vertical heights are simplified, the horizontal distance between the centre of each core is drawn to scale.
The benefit of studying the sulfate ecosystem is that the biological components that are contributing organic matter to the system are still in place and can be analysed alongside the mineral layers. Figure 6.31 shows the system with all of the biological materials removed, only the mineral layers and the organic matter found within them are shown. The nodule at the top of core 6 is not shown as it appeared to be an anomalous high point and the very thin iron oxide layer could not be separated from the moss and other biological materials. The majority of the system is characterised by a quartz sand containing clay and minor microcline and jarosite. In these materials organic detection is poor. The materials adjacent to the acidic stream that passes between cores 6 and 7 appear enriched in jarosite suggesting substantial alteration by acidic waters. The organic response during pyrolysis for these layers is also poor but the confounding influence of jarosite at such high concentrations would be substantial.

The best response for organic matter is seen in the thin layers of goethite near the surface where jarosite is either absent or at low concentrations. The waterlogged nature of the sediments at this location likely promoted the reactions that decompose jarosite and vulcanise organic matter. Thiophenes, aromatic compounds and polycyclic aromatic hydrocarbons are detected in cores 4 and 5. Though jarosite rich outcrops on Mars are evidence of acidic waters, the wet environment may only have persisted for a short while. A longer duration of liquid water would cause a fraction or the entirety of jarosite to decompose into goethite. In the sulfate ecosystem, and perhaps on Mars, the goethite that forms from decomposing jarosite appears to retain organic matter. Goethite is a far less aggressive oxidant during pyrolysis so analysis of goethite rich deposits in close proximity to jarosite units may be a potential route for analysing ancient martian acidic sulfur rich systems for organic matter.
6.7 Reassessing the natural jarosite clay for thiophene

The fact that when microbial activity is closely associated with a prolonged wet environment (where jarosite decomposes into goethite) much of the organic matter may be vulcanised is the most important observation from the sulfate ecosystem study. Thus when a sample containing both jarosite and goethite is pyrolysed the products should be examined for the presence of thiophene compounds. The natural jarosite clay collected at Brownsea Island contained 5% jarosite and 36% goethite (Chapter 3). The island is located over 20 km from St. Oswald’s Bay and the samples were collected a year apart so the differences in setting make it an ideal test sample to see if the findings from the sulfate ecosystem can be applied to other localities. Analysis of the pyrolysis products of the natural jarosite clay using a DB-5 column revealed only a minor peak for benzene (Chapter 3). The GS-Q column used to study carbon dioxide, oxygen and sulfur dioxide is only suitable for studying light gases but this includes molecules such as benzene and thiophene. The results from the natural jarosite clay

![Graph](image_url)

**Figure 6.32.** Peak areas for benzene and toluene for pyrolysis of natural jarosite clay samples at different temperatures. *Peaks are normalised to the sample mass before pyrolysis.*
decomposition experiments were re-examined and the peaks for mass to charge ratio (m/z) 78 (benzene) and m/z 84 (thiophene) were extracted from the original data (Figure 6.32).

Peaks for m/z 91 (toluene) and m/z 97 (methylthiophene) were searched for but no clear peaks were detected. Benzene and thiophene were both first detected at 500 °C and showed an increase with temperature up to 800 °C. At higher temperatures benzene showed a slight increase but thiophene showed a slight decrease. This may be related to sample heterogeneity or higher temperatures may impede the detection of thiophene relative to benzene.

Thiophene was not detected in the solvent extract of the natural jarosite clay, the only sulfur containing compound was benzenesulfonamide, which was interpreted as contamination. Vulcanised organic matter forms a large sulfur linked network that would be either insoluble or poorly soluble (Kowalewski et al., 2010). The lack of detection of indigenous sulfur containing compounds in the natural jarosite clay using dichloromethane-methanol extraction is therefore not unexpected.

6.8 Implications and discussion

Acidic sulfate-forming conditions are thought to have been common during the Hesperian on Mars (Bibring et al., 2006). A substantial part of Mars’ stratigraphy may therefore contain jarosite and any mission landing in Hesperian terrains will have to consider how best to analyse such materials. Jarosite has already proven a useful palaeoenvironmental indicator for Mars rovers such as Opportunity and Curiosity (Klingelhofer et al., 2004; Morris et al., 2006; Rampe et al., 2015).
The findings of this project show that jarosite forming in a prolonged wet environment will partially or completely decompose to goethite but the iron oxide may retain the organic matter that was present in the jarosite. A pristine jarosite outcrop is evidence of acidic aqueous alteration but water may not have persisted long enough to support potential martian microbial communities. An outcrop where low concentrations of jarosite are accompanied by high concentrations of goethite should be considered an ideal target for evolved gas analysis. A detection of thiophenes on Mars would not be conclusive evidence of indigenous organic matter as thiophenes have been found in meteorites (Sephton et al., 2005) but any detection of thiophenes on Mars would be highly significant and would warrant further investigations by more advanced methods such as the GC-MS and wet chemistry experiments available on Curiosity. Ferric oxides are often closely associated with sulfate-rich layered deposits in locations such as Valles Marineris and Terra Meridiani (Map 2; Map 4) (Bibring et al., 2007). The aqueous history of Meridiani Planum (Map 2), where Opportunity rover is operating, remains debated and the dominance of haematite in this locations suggests that if the Meridiani jarosite was associated with goethite further processing of the iron oxide has taken place (Bibring et al., 2007).

XRD analyses allow the cation content of jarosite crystals to be estimated. As demonstrated in this project analysing the cation chemistry of jarosite can be valuable for discerning the origin of different jarosite outcrops and the types of fluids that formed the crystals. The full data for the jarosite deposits found in the Pahrump Hills are not yet available but it is hoped that the CheMin instrument on board MSL will provide new insight into the fluids that formed jarosite in this region of Mars. Any mission travelling to a region of Mars where jarosite is
expected should ideally carry an XRD instrument, if feasible within the constraints of the payload capacity.

6.9 Conclusions

A series of cores were taken from across the acidic sulfate ecosystem first discovered on field work in St. Oswald’s Bay, Dorset, in 2012. The variation in mineralogy and organic chemistry across the study site was assessed. Much of the surface and subsurface consisted of a quartz sand with varying amounts of clay minerals, microcline and jarosite. Pyrolysis of these units typically produced only simple organic molecules such as benzene and toluene. In waterlogged sediments in the centre of the study area the surface was capped with a goethite crust and a microbial mat. The goethite produced a greater diversity of organic compounds during pyrolysis than the sandy-clays, with the products including thiophenes. The thiophenes are inferred to have been produced by natural vulcanisation reactions during the decomposition of jarosite into goethite. This result suggests that goethite in close proximity to jarosite on Mars may represent evidence for prolonged aqueous alteration. Goethite may perhaps be the most accessible mineralogical record of any potential sulfate ecosystem on Mars as goethite is a significantly less aggressive oxidant during pyrolysis experiments than jarosite. Additionally the importance of XRD analyses of jarosite deposits was highlighted as unit cell modelling during phase quantification allowed the identification of two distinct jarosite forms. A potassium-rich group, into which most of the samples fit, and a sodium-rich type, which was formed by sea spray. The mineral crust produced by sea spray yielded organochlorines during pyrolysis, this was interpreted to be due to organochlorines in seawater and not a mineral-organic compound interaction during pyrolysis.
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Mars global image from NASA/JPL-Caltech (2013)
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7.1 The oxidising potential of jarosite during thermal extraction

Missions to Mars have revealed that there were periods of significant water activity in the planet’s early history, which eroded landscapes and produced characteristic deposits such as conglomerates (Golombek et al., 1997a; Ehlmann et al., 2011; Yingst et al., 2013). Though liquid water can no longer persist on the martian surface, water is still present on the planet in the form of hydrated minerals, the polar ice caps and subsurface ice deposits (McEwen et al., 2007; Milliken et al., 2008; Arvidson et al., 2009; Hecht et al., 2009; Lichtenberg et al., 2010). Many of the missions that have landed on the martian surface have returned data that suggest that some ancient environments were habitable for life (Grotzinger et al., 2012; Mahaffy et al., 2012; Williams et al., 2013; Vaniman et al., 2014). Observations from orbit show that much of Mars is layered and that these layers exhibit compositional variation, with certain regions appearing to have been exposed very recently (Malin & Edgett, 2001; Christensen et al., 2003). Volcanism and aeolian erosion have delivered heat and transported and mixed materials around the surface for much of Mars’ existence (Hanel et al., 1972; McCauley, 1973; Hartmann, 1999). The active geological history of the planet in combination with its relative proximity to Earth makes Mars a promising test case for investigating whether life could have evolved on other worlds.

The geological history of Mars is characterised by three stratigraphic systems, the ancient Noachian, in which clay-forming conditions dominated, the transitional Hesperian, in which sulfate-forming conditions took over and the present day Amazonian, which is characterised by anhydrous ferric oxides (Tanaka, 1986; Bibring et al., 2006). Analysing the geology of proposed landing sites on Mars is complicated by the fact that much of the surface is mantled in a covering of fine dust that can obscure metre scale features (Keszthelyi et al., 2008).
Missions to the surface should therefore be as prepared as possible for previously unrecognised features or deposits that may present challenges for the operation of lander or rover experiments.

The technological and financial constraints of a mission payload has led to thermal extraction being the most popular method to search for organic compounds on the surface of other planetary bodies (Biemann et al., 1977; Guinn et al., 2008; Mahaffy et al., 2012). Attempting wet chemistry on other worlds is extremely difficult, not only due to the engineering challenges, but because minerals can have a profound influence on the performance of solvents and solutions (Biemann et al., 1977; Stalport et al., 2012). Thermal extraction is also susceptible to mineral effects (Saiz-Jimenez, 1994; Faure et al., 2006; Ming et al., 2009; Lewis et al., 2015). The fact that organic matter detection missions have so far only detected simple organochlorine compounds is suggested to be related to the presence of chlorine and oxygen containing salts, known as perchlorates, on the surface of Mars (Ming et al., 2009; Glavin et al., 2013). Perchlorates thermally decompose at relatively low temperatures and release chlorine and oxygen (Shimokawabe et al., 1977; Devlin & Herley, 1986). They appear to be globally spread and their presence greatly complicates the interpretation of data from thermal experiments on Mars (Ming et al., 2009; Catling et al., 2010; Glavin et al., 2013). The diverse geology of Mars highlights the importance of identifying all the mineral species that might interfere with thermal extraction experiments. The more comprehensive our understanding of problematic minerals the more informed and rapid decision making can be when these species are encountered on Mars.

Volcanic outgassing during the Hesperian released large volumes of sulfur dioxide into the atmosphere, which led to sulfate-rich acidic conditions (Bibring et al., 2006). Such conditions
would have promoted the formation of the iron sulfate mineral jarosite (Stoffregen et al., 2000; Papike et al., 2006). Iron sulfates are known to decompose at around the temperatures used to liberate fragments of macromolecular material from samples (Mu & Perlmutter, 1981; Sephton & Gilmour, 2001; Sephton et al., 2004; Frost et al., 2005a; Navarro-González et al., 2006; Sephton, 2012; Sephton et al., 2013). Despite this, there has been very little research into the potential of jarosite to disrupt organic matter detection through thermal extraction. Hesperian terrains make up 34% of the surface of Mars so understanding the influence of jarosite on thermal experiments will be relevant for the analysis of a large proportion of Mars’ geological history (Croswell, 2003).

The experiments described in this thesis used natural jarosite containing samples and synthetic potassium and sodium jarosite to greatly improve our appreciation of the potential for jarosite to disrupt thermal extraction on Mars. Samples were characterised by quantitative X-ray diffraction (XRD) and thermal decomposition was studied by pyrolysis-gas chromatography-mass spectrometry (py-GC-MS). A natural jarosite clay collected from Brownsea Island, Dorset, UK, was found to contain 5% jarosite. Solvent extraction and acid washing were used in combination with elemental analysis-isotope ratio mass spectrometry (EA-IRMS) to characterise the inorganic and organic carbon in the natural jarosite clay. The natural jarosite clay was found to be carbonate free and contained 0.45% organic carbon, a proportion of which was extractable organic matter. However, pyrolysis of the natural jarosite clay produced only a very weak peak for benzene with major peaks for sulfur dioxide, carbon dioxide, carbon monoxide and water. Further experiments proved that the carbon dioxide and carbon monoxide were a result of the oxidation of organic matter caused by oxygen released from jarosite decomposition. Oxidation was seen to be substantial at the
temperatures used to study macromolecular organic matter, which prevented the detection of organic matter other than the very weak peak for benzene.

Synthetic jarosite samples allowed the production of oxygen from jarosite decomposition to be observed directly without the complicating influence of other minerals or organic matter. During stepped pyrolysis experiments between 300 °C and 1000 °C substantial sulfur dioxide peaks were seen that were accompanied by oxygen. Cumulative measurements showed that jarosite decomposition produces sulfur dioxide and oxygen at a 2:1 ratio. Other reactions occurring during the decomposition of the jarosite structure did not act as a sink for oxygen indicating that sulfate sourced oxygen from jarosite is free to react with organic matter or other phases.

Natural potassium-rich and sodium-rich forms of jarosite were collected from St. Oswald’s Bay, Dorset, UK. Together with potassium-rich and sodium-rich synthetic forms the variation in decomposition profiles between different forms of jarosite was assessed. Potassium jarosite was seen to begin to decompose to release sulfur dioxide and oxygen at lower temperatures than sodium jarosite, but the temperature difference was much greater in the synthetic samples relative to the natural materials from St. Oswald’s Bay. These results highlight the difficulty of synthesising analogues to jarosite formed in natural low temperature acidic systems, which may have many impurities and may be poorly crystalline. The peaks for sulfur dioxide and water (with water formed by the dehydroxylation of jarosite) were seen to shift to lower temperatures if the jarosite was potassium rich or to higher temperatures if the jarosite was sodium rich. In simple mixtures this behaviour could be used to differentiate different forms of jarosite by evolved gas analysis. In more complex mixtures however the interactions between different phases makes interpreting temperature profiles
much more complicated. For example, to deconvolve the decomposition products of the natural sodium jarosite rich sample an analogue mixture of laboratory standards was pyrolysed. It was found that the thermodynamics of carbonate decomposition were influencing the decomposition temperature of jarosite.

Pyrolysis of mixtures of synthetic jarosite and the organic plastic polyethylene at 650 °C enabled the influence of jarosite on organic molecule detection to be analysed directly. When polyethylene is pyrolysed as a single phase a series of dienes, alkenes and alkanes are produced. When mixed with either sodium jarosite or potassium jarosite the peaks for dienes and alkenes were dramatically reduced while the peaks for alkanes were largely unchanged. Jarosite related oxidation not only reduces the response for organic matter, it also complicates the interpretation of the species that are detected.

Jarosite and polyethylene mixtures were also heated at 500 °C, a temperature at which jarosite decomposition should be minimal but some organic molecules should still be liberated from the polyethylene. Pyrolysis of polyethylene as a single phase at 500 °C produced a series of small peaks for alkenes and alkanes. When mixed with jarosite the peaks for the alkenes and alkanes were seen to increase slightly. Comparing the sulfur dioxide production from jarosite when pyrolysed as a single phase relative to when mixed with polyethylene showed that mixing lowered the decomposition temperature of jarosite. Despite the enhanced jarosite decomposition the oxygen released appeared to somewhat aid the liberation of organic matter at lower temperatures. The natural jarosite containing samples from St. Oswald’s Bay were pyrolysed at 500 °C and 650 °C. The natural sodium jarosite rich sample was found to be very poor in organic matter but the potassium jarosite rich sample produced peaks for benzene, toluene and acetic acid at both temperatures. There
was little difference between pyrolysis at 500 °C and 650 °C for the potassium jarosite rich sample suggesting that pyrolysis of jarosite containing materials at the non-standard temperature of 500 °C should be investigated further.

Sulfur dioxide was first detected during in situ evolved gas analysis on Mars when the aeolian Rocknest samples were analysed by Curiosity, which suggests jarosite was not present at the Viking and Phoenix landing sites (Map 1) (McAdam et al., 2014). Jarosite and iron sulfate were inferred as possible minor phases in the Rocknest materials (Leshin et al., 2013). However, any carbon dioxide that might have been produced by oxidation related to jarosite decomposition would have been obscured by a substantial carbon dioxide peak that was inferred to be related to carbonate decomposition (Leshin et al., 2013). Recently Curiosity discovered jarosite, in an area named the Pahrump Hills, at concentrations great enough to be detectable to the on board X-ray diffraction instrument; Chemistry and Mineralogy (CheMin) (Rampe et al., 2015). The full data for the Pahrump Hills samples are not yet published but the temperature profiles for the major volatiles released by one of the samples (Confidence Hills) shows a major sulfur dioxide peak at around 600 °C (Franz et al., 2015). This agrees well with the behaviour of jarosite seen in the results discussed in Chapter 4. A high temperature sulfur dioxide shoulder seen in the Confidence Hills data (Franz et al., 2015) appears similar to the sulfur dioxide peaks produced by magnesium sulfate in the experiments described in Chapter 4. A high temperature carbon dioxide peak was also seen in the Confidence Hills data, which could potentially be related to the combustion of highly refractory organic matter (McAdam et al., 2015). The decomposition of a carbonate such as calcite is an alternative explanation for the Confidence Hills high temperature carbon dioxide but until the full data are published such assertions are purely speculative.
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7.2 Carbon dioxide, organic matter and molecular weight

The results presented in Chapters 3 and 4 of this thesis show that jarosite should be added to the list of problematic minerals for thermal extraction on Mars alongside perchlorates. Subsequently it was investigated as to whether the carbon dioxide resulting from oxidation of organic matter by perchlorate and/or jarosite could still be used to interpret the nature of organic matter in a sample. Low molecular weight organic matter is typical of highly mobile species that are often contaminants. High molecular weight organic matter is typical of indigenous materials. The higher the molecular weight of organic matter the higher the decomposition temperature.

Low and medium molecular weight organic matter was represented by maltene and asphaltene fractions from an oil sample while solvent extracted coal represented high molecular weight organic matter. The low and medium molecular weight samples were mixed with perchlorate and the high molecular weight with perchlorate and/or jarosite. Carbon dioxide peaks were seen to broaden and occur at higher temperatures when the oxidising salts were mixed with increasingly higher molecular weight organic matter. The carbon dioxide detected correlated with the production of carbon monoxide, hydrochloric acid and organochlorines when mixed with perchlorate. These findings were applied to results from Curiosity analyses within Gale Crater (Map 3). The carbon dioxide produced from the Rocknest windblown dust sample was found to likely be from an inorganic source while the Sheepbed mudstone appeared to host low molecular weight organic matter.

When jarosite was mixed with coal and pyrolysed without perchlorate a sharp high temperature carbon dioxide peak was seen that correlated with carbon monoxide and small peaks for benzene, toluene, ethane and propane. Interestingly, when coal, jarosite and
perchlorate were mixed a difference response for organochlorines was seen compared to pyrolysis of just coal and perchlorate. Only when jarosite was mixed with coal and perchlorate was chlorobenzene detected in the pyrolysis products. Though carbon dioxide can be indicative of molecular weight the interpretation of associated organochlorines and organic matter is complicated if multiple oxidising salts are present in a mixture.

7.3 Jarosite and goethite: The search for Hesperian organic matter

While perchlorate appears to be globally spread, and therefore an issue in the majority of thermal experiments carried out on surface materials on Mars, jarosite is typically restricted to sulfate-rich outcrops (Klingelhofer et al., 2004; Archer et al., 2013; Glavin et al., 2013; Rampe et al., 2015). However, simply avoiding jarosite would be an unsatisfactory mitigation step as jarosite is indicative of acidic sulfate-rich waters that can support thriving ecosystems on Earth (Arvidson et al., 2010).

During sampling in St. Oswald’s Bay a small biologically-active acidic stream was discovered in which jarosite was precipitating and some adjacent surfaces were covered in iron oxide and a fibrous microbial mat. The location represented an ideal test case for examining the mineralogical and organic compound variation across a jarosite forming system. A series of cores were taken across the stream and subdivided into layers, which allowed the vertical and horizontal variation to be studied. While previous experiments involved the use of discrete samples the work in this project was closest to the sampling opportunities available to rovers and landers on Mars.

The majority of the system was made up of a quartz sand with minor clay minerals, feldspar and jarosite. Py-GC-MS detected only a very weak response for organic matter from these layers. Close to the stream the cores were enriched in jarosite and also gave a very poor
response for organic matter but this was expected as the high abundance of jarosite would have released a great deal of oxygen during heating. The waterlogged soils in the centre of the system consisted of quartz sands hosting jarosite and capped by a layer of goethite. Py-GC-MS of the goethite layers detected multiple organic compounds, including thiophenes. Jarosite only persists on geological timescales in extremely arid environments and in the continued presence of water it decomposes to goethite. The findings from the sulfate ecosystem in St. Oswald’s Bay indicate that organic matter initially preserved in jarosite is partially retained despite the mineralogical changes of jarosite decomposing to goethite. During the decomposition of jarosite sulfur is released and the liberated sulfur appeared to be involved in natural vulcanisation reactions with the organic matter.

A reassessment of the pyrolysis results from the goethite containing natural jarosite clay from Brownsea Island indicated that thiophenes were also present in this material. Goethite is significantly less oxidising during pyrolysis relative to jarosite and the mineral may represent an ideal target for attempting to sample the organic chemistry of jarosite forming systems on Mars. Pristine jarosite is evidence of a brief period of aqueous alteration while goethite in close association with jarosite is indicative of longer lasting wet conditions, which would have been more beneficial to life. The detection of thiophenes in goethite deposits on Mars would be possible evidence of vulcanised indigenous organic matter and warrant further investigations by other experiments, such as the GC-MS and wet chemistry experiments available in the Sample Analysis at Mars instrument on Mars Science Laboratory.

In all of the projects described in this thesis the availability of X-ray diffraction data for the samples greatly aided the interpretation of jarosite. Quantifying the phases within the jarosite containing samples allowed the unit cell of jarosite, and therefore the abundance of
potassium, sodium and hydronium to be estimated. Knowing the cation content of jarosite allowed the fluids that formed the minerals to be inferred and in the sulfate ecosystem this permitted the differentiation of jarosite deposits formed by potassium rich groundwaters from jarosite formed by sea spray. Combining thermal experiments with the ability to perform XRD, as Mars Science Laboratory does, allows detailed studies of jarosite containing materials to be performed.

7.4 Further work
The large number of samples acquired from the acidic stream in St. Oswald’s Bay encouraged collaborations with other researchers. The materials are being used to investigate the effectiveness of other techniques such as subcritical water extraction and pyrolysis-fourier transform infrared spectroscopy for analysing the samples. In addition, a comprehensive study of the organic chemistry of the system will be carried out using Bligh-Dyer extraction on the mineral layers collected in this work, as well as the individual layers and water samples collected in 2013.

Pyrolysis of jarosite-rich samples at 500 °C was seen to potentially allow a proportion of the organic matter in a sample to be liberated while minimising jarosite decomposition. Pyrolysing the jarosite rich materials found in the sulfate ecosystem at 500 °C would allow this theory to be tested further. Identifying a pyrolysis temperature at which jarosite containing samples can be analysed effectively for organic matter would be beneficial for the operation of Mars thermal extraction experiments operating in jarosite rich areas.

The results from the pyrolysis study of the sulfate ecosystem indicated that pyrolysing goethite layers is a potential route for sampling organic matter in jarosite forming systems through thermal extraction. If further field work is conducted in the area it would be of great
interest to perform high resolution sampling of the fine goethite layers seen in core 7 at St. Oswald’s Bay and at nearby Stair Hole. Identifying other sites on Earth that host goethite in close association with jarosite and testing the organic preservation in these iron oxide layers would further test the theory that goethite is the best way to analyse the organic matter of preserved jarosite forming systems.
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Appendix 1 – Calibration curves
Sulfur dioxide calibration curve

\[ y = 5,625,165,771,685.20x \]

\[ R^2 = 0.94 \]
Carbon dioxide calibration curve

\[ y = 4.784 \times 10^2 \times 2.942 \times 10^4 \times x \]
\[ R^2 = 0.69 \]
Oxygen calibration curve

\[ y = 3,780,159,326,726.78x \]
\[ R^2 = 0.99 \]
Appendix 2 – X-ray diffraction data
St. Oswald’s Bay – Decomposed pyrite nodule (GS)
St. Oswald’s Bay – Jarosite from the acidic stream (PRT)
Lake District – Material from the upper mine dump

Quartz, hemimorphite, smithsonite, anatase, illite, montmorillonite.
Sulfate ecosystem - BCT Clay from top of core
Sulfate ecosystem — SHR Rusty crust in middle of core