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Regular article

Investigating the history of volatiles in the solar system using synchrotron infrared micro-spectroscopy

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A B S T R A C T

The aqueously altered CM carbonaceous chondrite meteorites can be used to investigate the nature and transport of volatiles in the early solar system. We present the preliminary results of an effort to collect 2D infrared (IR) spectral maps from the matrix and fine-grained rims (FGRs) of material that surround chondrules and inclusions in the Murchison CM2 meteorite using synchrotron IR micro-spectroscopy. The main features in mid-IR spectra of the matrix and FGRs occur at ~3500 cm⁻¹ and ~1000 cm⁻¹ and are attributed to −OH/H₂O and Si−O bonds in phyllosilicates and anhydrous silicates. Minor features in the spectra are attributed to organic species (3000–2800 cm⁻¹), CO₂ (2400–2000 cm⁻¹), and carbonates (1500–1380 cm⁻¹). In both the matrix and FGRs we observe correlations between the −OH/H₂O and phyllosilicate/silicate features confirming that phyllosilicates dominate the mineralogy. This is consistent with previous studies showing that Murchison contains ~70 vol% phyllosilicates following aqueous alteration on an asteroid parent body. The presence of anhydrous silicates in the matrix indicates that the alteration was heterogeneous at the micron-scale and that the reactions did not reach completion. We highlight a possible correlation between the phyllosilicates and organic species in the matrix, supporting the hypothesis that phyllosilicates may have played an important role in the formation and preservation of simple organic molecules and compounds. In the FGRs variations in the distribution of the phyllosilicate minerals crenstondite and Mg-serpentine/saponite likely reflect differences in the local geochemical conditions during aqueous alteration on the asteroid.

1. Introduction

Primitive meteorites provide a glimpse into the processes and events that have shaped our solar system over the last ~4.5 billion years. The CM (“Mighei-type”) carbonaceous chondrite meteorites consist of calcium-aluminium-rich inclusions (CAIs), chondrules and silicate fragments set within a matrix (> ~50 vol%) of phyllosilicates, oxides, sulphides and carbonates. They contain ~10 wt% extra-terrestrial H₂O and are interpreted as the products of low temperature (< 100 °C) aqueous alteration after ices melted on a water-rich asteroid parent body [1]. Asteroids may have delivered water to the terrestrial planets through aqueous alteration after ices melted on a water-rich asteroid parent body and are interpreted as the products of low temperature (< 100 °C) tailed mineralogical and chemical studies is challenging due to the fine grainsize (< 1 µm) of the matrix. Furthermore, the CM chondrites experienced varying degrees of aqueous alteration and many are re-golith breccias, resulting in heterogeneous textures. Consequently, it is spatially resolved micro- and nano- techniques that are likely to provide the most comprehensive picture of the aqueous reactions on asteroids.

Several studies have used infrared (IR) spectroscopy to characterise anhydrous and hydrous phases in CM chondrites [3–6]. Often these have focused on bulk samples or extracted matrix where the spatial relationship between the phases has been lost. Synchrotron IR micro-spectroscopy is a non-destructive technique that can be used to collect high signal-to-noise IR spectra at high spatial resolution whilst maintaining the petrographic context of the sample. Importantly, the IR spectra can be spatially correlated with mineralogical and chemical data obtained using other imaging and analytical techniques such as optical and electron microscopy, X-ray fluorescence (XRF), X-ray diffraction (XRD) and X-ray absorption near-edge structure spectroscopy (XANES).

Synchrotron IR micro-spectroscopy has previously been used to...
study the mineralogy and organic component of meteorites, interplanetary dust particles (IDPs), and samples returned by NASA’s Stardust mission [7–13]. Many of these studies were performed in transmission mode. Here, we present the preliminary results of an effort to collect 2D IR spectral maps in reflectance mode from a polished section of the Murchison CM chondrite meteorite. Our aims with this work were to image the spatial distribution of hydrates species and phases, differentiate between phyllosilicate compositions, and subsequently to try and infer differences in the degree and timing of aqueous alteration across distinct mineralogical micro-textural features in the CM chondrites.

2. Experimental

2.1. Sample

The Murchison CM chondrite fell in Australia in 1969 with a total recovered mass of > 100 kg. It is classified as a petrologic type 2 meteorite having experienced extensive aqueous alteration and contains ~70 vol% phyllosilicates, ~25 vol% anhydrous silicates plus minor (< 5 vol%) magnetite, pyrrhotite and calcite [14]. Partially hydrated CAIs and chondrules are usually surrounded by compact fine-grained rims (FGRs) of hydrated minerals that in backscattered electron (BSE) images are distinct from the matrix [15,16]. Aqueous alteration of CM chondrites is interpreted to have taken place on an asteroid parent body, although it has been suggested that the FGRs could have formed through hydration of silicate dust in the nebula prior to accretion [15]. Murchison also has ~2 wt% carbon, most of which is organic material that can be divided into soluble and insoluble fractions [17].

We studied a demountable polished thick (~100 µm) section of Murchison. Prior to collecting IR spectral maps we characterised areas of matrix and FGRs using a Zeiss Evo 15LS scanning electron microscope (SEM) at the Natural History Museum (NHM) (Fig. 1), London, and μXRD, μXRF and Fe-μXANES on beamline 11B at Diamond Light Source (DLS), UK [18].

2.2. Synchrotron IR spectroscopy

IR spectral maps were acquired from one matrix area and three FGRs in Murchison on the MIRIAM beamline (B22) at DLS [19]. The end-station comprised a Bruker Hyperion 3000 IR microscope coupled with a Bruker Vertex 80 V Fourier transform IR (FTIR) spectrometer, a high-sensitivity, mid-band MCT liquid N₂ cooled detector, and a broadband KBr beamsplitter.

The 2D IR spectral maps ranged from 80 µm × 80 µm to 100 µm × 100 µm in size and were obtained in reflection geometry, in a confocal mode with 8 × 8 µm effective back aperture and 5 × 5 µm effective slit size after the sample, 256 scans per point, and a spectral resolution of 4 cm⁻¹. Step sizes were varied as a function of the overall size of the map ensuring 1–2 µm oversampling, with respect to the slit size. The spectral range of this study was from ~3900 cm⁻¹ to ~800 cm⁻¹, limited by the CaF₂ windows in the long wavelength region. Gold foil was used for the collection of a background spectrum.

In order to minimise the effects of absorbed terrestrial water the polished section was mounted horizontally within a Linkam heating stage, which was sealed using CaF₂ windows above and below the sample, and purged with a constant flow of dry ultra-pure N₂ gas. The IR spectral maps were collected initially at room temperature, and then again at 100 °C, 200 °C and 300 °C, with a minimum of 30 min equilibration time at each elevated temperature.

3. Results

Fig. 2 shows examples of IR spectra collected at room temperature and 300 °C for a FGR in the Murchison meteorite. Spectra from the matrix are very similar to the FGRs. The main features occur at ~3500 cm⁻¹ and ~1000 cm⁻¹ and are attributed to –OH/H₂O and Si–O bonds, respectively. This is consistent with the mineralogy of Murchison, which is known to contain both hydrous Fe- and Mg-rich phyllosilicates and anhydrous silicates (olivine and enstatite), and is also in good agreement with previous IR studies of CM chondrites [3–6]. Minor features in the spectra are attributed to organic species (3000–2800 cm⁻¹) and carbonates (1500–1380 cm⁻¹). Atmospheric CO₂ is also present (2400–2200 cm⁻¹) and not related to the meteorite. In order to investigate the spatial distribution of different components in the matrix and FGRs, for each point in a map we integrated under the feature of interest using the spectral ranges provided by [10,11] (Table 1).

Fig. 2 also demonstrates how heating the sample (up to 300 °C) altered the IR spectra. In particular, absorbed terrestrial water was removed from the sample surface causing a change in the shape and intensity of the –OH/H₂O feature [e.g. 4], while the organic feature decreased in intensity due to the modification and/or potential destruction of different species. All other features in the spectra remained essentially the same with sample heating.

Fig. 3 shows how the distribution of –OH/H₂O, phyllosilicates/silicates (spectra collected at 300 °C) and organic species (spectra collected at room temperature) varies within a matrix region of the Murchison meteorite. The –OH/H₂O and phyllosilicate/silicate features are broadly correlated, which is consistent with the presence of abundant –OH/H₂O-bearing phyllosilicates. We also observe a possible correlation between the –OH/H₂O and organic features (note that the maps cover the same area but were collected at different temperatures), hinting that the phyllosilicates are spatially related to the organic species in CM chondrites. However, the maximum intensity of the phyllosilicate/silicate feature actually occurs at the minimum intensity of the –OH/H₂O feature suggesting that some anhydrous silicates escaped significant aqueous alteration.

The mineralogy of the Murchison meteorite is known to be dominated by phyllosilicates of differing composition including the Fe-rich serpentine cronstedite (~50 vol%) and Mg-rich serpentine/saponite (~20 vol%) [14]. The strongest features for cronstedite and Mg-rich serpentine/saponite occur at ~930 cm⁻¹ and ~1000 cm⁻¹ respectively [e.g. 5,20], so to further investigate spatial variations in the composition of the phyllosilicates in the matrix we also generated images at these modes (integrated with a spectral width of 50 cm⁻¹ using a local linear baseline, images not shown). We find that the images at these modes are very similar and are also correlated with the –OH/H₂O feature.

Fig. 4 shows the distribution of –OH/H₂O and phyllosilicates/silicates features (spectra collected at 300 °C) in a FGR surrounding an olivine chondrule fragment within the Murchison meteorite. There are four distinct regions of varying –OH/H₂O content; the region of lowest intensity correlates with the anhydrous olivine fragment, while the remaining areas are all within the FGR and in general correlate with the phyllosilicate/silicate features. This implies that the mineralogy of the FGR is comprised mainly of –OH/H₂O-bearing phyllosilicates. Images generated at ~930 cm⁻¹ and ~1000 cm⁻¹ show a bi-modal distribution of the phyllosilicates, with cronstedite found within the outer regions of the FGR, and Mg-serpentine/saponite within the inner rim at the interface with the olivine chondrule fragment (Fig. 5).

4. Discussion

The IR spectral maps demonstrate that the matrix of the Murchison CM2 meteorite analysed in this study is dominated by the phyllosilicate minerals cronstedite and Mg-rich serpentine/saponite. This is not surprising as Murchison is known to contain ~70 vol% phyllosilicates that formed during a period of aqueous alteration on its asteroid parent body. Due to its large surface-area-to-volume ratio the fine-grained matrix was more susceptible to hydration and subsequently altered before the CAIs and chondrules. Metal and Fe-rich olivine were the first
phases to be altered producing Fe-rich fluids from which cronstedtite formed. As aqueous alteration continued the supply of Fe-rich phases became exhausted and increasingly Mg-rich minerals were attacked by the fluids, resulting in the formation of Mg-rich serpentine/saponite. That we observe randomly intermixed cronstedtite and Mg-rich serpentine/saponite in the matrix of Murchison suggests an extensive degree of aqueous alteration. However, the presence of anhydrous silicates in the matrix indicates that the alteration was heterogeneous at the micron-scale, and that at least locally the reactions did not reach completion, possibly due to the availability of fluids.

In the matrix we observe a possible correlation between the distribution of the phyllosilicates and organic species. However, we advise caution when making this link as the IR maps were collected after analyses on beamline I18 at DLS using a 14 keV X-ray beam that potentially modified or destroyed any organics in the sample. Nevertheless, synchrotron IR micro-spectroscopy is one of the few analytical techniques capable of examining this relationship in-situ at high spatial resolution and similar associations between phyllosilicates and organics have recently been identified using this method in the primitive ungrouped carbonaceous chondrite Tagish Lake [12] and the CR2 carbonaceous chondrite NWA 852 [11]. In the CM chondrites several studies have reported a relationship between organics and phyllosilicates at the nano-scale [22,23], and although still in its early stages this work lends further support to the hypothesis that phyllosilicates played a crucial role in the synthesis and preservation of simple organic molecules and compounds on asteroids in the early solar system.

The IR spectral maps confirm that the FGRs contain abundant phyllosilicates, but in contrast to the matrix we observe a bi-modal distribution of cronstedtite and Mg-rich serpentine/saponite. The Mg-rich serpentine/saponite dominates the inner region of the FGR, in direct contact with the olivine chondrule fragment, and the cronstedtite occurs in the outer regions of the FGR, in contact with the matrix. The bi-modal distribution of the phyllosilicates could be explained if alteration of the outer rim was by Fe-rich fluids produced through hydration of the Fe-rich matrix, whereas the inner rim was altered by more Mg-rich fluids due to hydration of the Fe-poor olivine chondrule fragment. In this scenario aqueous alteration of the FGR took place on the asteroid parent body and not in a nebula environment.

In atomistic terms, simplifying the crystal chemistry of the two minerals and considering the $\sim$OH ion a single ‘atomic’ species, then cronstedtite comprises about 30% $\sim$OH, whereas Mg-serpentine/saponite has a maximum of $\sim$10%. Thus it might be expected that the areas with the most intense $\sim$OH/H$_2$O feature might contain more cronstedtite than Mg-serpentine/saponite. This is broadly true, although not entirely consistent with our observations of three distinct regions of varying $\sim$OH/H$_2$O content within the FGR (see Fig. 4). It is possible that the relative intensities of the $\sim$OH/H$_2$O feature are being influenced by either non-stoichiometric proportions of $\sim$OH within the minerals or the distribution of other components such as organic species and the complex mineral tochilinite, a mixed-layer phase comprising Fe$_{1-x}$S and Mg(OH)$_2$ layers known to occur in the Murchison CM chondrite [e.g. 14].

We note that the mineralogical zoning identified within the FGR is consistent with the $\mu$XRD, $\mu$XRF and Fe-$\mu$XANES data collected from exactly the same area of the FGR [18]. Subtle zoning in the
concentration of Fe was revealed by µXRF mapping, and systematic variations in spectral features of the Fe-µXANES data were seen across the bi-modal distribution of cronstedtite and Mg-rich serpentine/saponite identified within this study.

Finally, we anticipate that synchrotron IR micro-spectroscopy will be a powerful tool for investigating samples returned from the surfaces of bodies in space. For example, within the next five years the JAXA Hayabusa-2 and NASA OSIRIS-REx missions will return to Earth with primitive asteroidal materials that may be similar to CM chondrites like Murchison. Infrared maps can provide mineralogical information without destroying precious sample material, enabling the spectra to be spatially correlated to data collected by other analytical techniques and directly compared to that acquired remotely in space.

5. Summary

The aqueously altered CM carbonaceous chondrite meteorites are physical samples of water-rich asteroids that offer a direct probe into the characteristics of volatile reservoirs in the solar system. However, the fine-grained and heterogeneous nature of CM chondrites makes them challenging to study in-situ using optical and electron microscopy. We present the preliminary results of an effort to collect 2D IR spectral maps from the matrix and FGRs in the Murchison CM2 meteorite using synchrotron IR micro-spectroscopy. In summary:

(1) Typical features in the mid-IR spectra of matrix and FGRs in the Murchison CM2 meteorite are attributed to −OH/H2O, Si–O, C–H and C=O bonds in hydrous phyllosilicates, anhydrous silicates, carbonates and organic species. The spatial distribution of these phases was investigated by integrating under the spectral range of interest, with the shaded boxes indicating the integration areas for cronstedtite and Mg-rich serpentine/saponite (see text and Table 1 for details). Note that the spectra are plotted in absorbance (for comparison to other IR spectroscopy studies) and are not directly comparable to remote sensing observations of asteroid surfaces.

Table 1

<table>
<thead>
<tr>
<th>Spectral Feature</th>
<th>Mode</th>
<th>Integration Range (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>−OH/H2O</td>
<td>H–O–H stretch</td>
<td>3600–3100</td>
</tr>
<tr>
<td>Organics</td>
<td>C–H stretch</td>
<td>3000–2800</td>
</tr>
<tr>
<td>H2O</td>
<td>H–O–H bend</td>
<td>1640–1660</td>
</tr>
<tr>
<td>Carbonate</td>
<td>C=O stretch</td>
<td>1500–1380</td>
</tr>
<tr>
<td>Phyllosilicate/Silicate</td>
<td>Si–O stretch</td>
<td>1100–800</td>
</tr>
</tbody>
</table>

Table 1 Integration ranges used to construct spatial distribution maps of hydrous phyllosilicates, anhydrous silicates, carbonates and organic species in FGRs and matrix within the Murchison meteorite.

Conflict of interest

The authors declared that there is no conflict of interest.
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