Investigating the shock histories of lunar meteorites Miller Range 090034, 090070, and 090075 using petrography, geochemistry, and micro-FTIR spectroscopy

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Abstract—Fourier transform infrared (FTIR) spectroscopy and cathodoluminescence (CL) imaging techniques, combined with electron microprobe analyses, have been used to determine the physical state of feldspathic phases that have been subject to varying levels of shock in the grouped lunar meteorites Miller Range 090034, 090070, and 090075. Six feldspathic phases have been identified based on spectral, textural, and chemical properties. A specific infrared wavelength band ratio (1064/932 cm\(^{-1}\) equivalent to 9.40/10.73 \(\mu m\)), chosen because it can distinguish between some of the feldspathic phases, can be used to estimate the pressure regimes experienced by these phases. In addition, FTIR spatial mapping capabilities allow for visual comparison of variably shocked phases within the samples. By comparing spectral and compositional data, the origin and shock history of this lunar meteorite group has been determined, with each of the shocked feldspathic phases being related to events in its geological evolution. As such, we highlight that FTIR spectroscopy can be easily employed to identify shocked feldspathic phases in lunar samples; estimate peak shock pressures; and when compared with chemical data, can be used to investigate their shock histories.

INTRODUCTION

The lunar crust has been extensively modified by impact bombardment of projectiles (e.g., asteroids and comets) since its formation (e.g., Melosh 1989; Ryder et al. 2000; Neukum et al. 2001; Ryder 2002; Stöffler et al. 2006; Hiesinger et al. 2011). It has been established that the cratering rate has decreased through time since the end of the period of basin-forming at around 3.8 Ga; however, the cratering rate prior to this time is largely unknown due to the “resetting” of lunar surface ages by widespread impact modification of the lunar crust (Spudis 1993). Since \(~3.8\) Ga, the Moon’s surface has been reworked by smaller impacts through time, resulting in “gardening” of the lunar regolith (Hörz and Cintala 1997; Neukum et al. 2001; Stöffler and Ryder 2001). The records of such impacts are preserved in the rocks and soils collected by the Apollo missions, in addition to recovered lunar meteorite samples.

Lunar meteorites represent material from random locations across the lunar surface, making them highly useful for investigating lunar surface and crustal processes (Palme et al. 1991; Korotev et al. 2003; Korotev 2005; Warren 2005; Nyquist et al. 2006; Joy et al. 2010; Joy and Arai 2013). By contrast, the Apollo suite of samples originates from specific locations on the lunar nearside that are limited to the Procellarum KREEP Terrane region, which is dominated by KREEP-rich lithologies with higher concentrations of incompatible trace elements (Jolliff et al. 2000). As such, lunar meteorites can provide a different perspective into the global diversity of crust formation and modification processes (Korotev 2005; Arai et al. 2011; Gross et al. 2014).
Both Apollo and lunar meteorite samples have undergone variable impact shock metamorphism as a result of high pressures and temperatures associated with impact events (Engelhardt et al. 1970; French 1998; Ohtani et al. 2010; Zhang et al. 2011; Miyahara et al. 2013; Darling et al. 2016). Effects range from total melting to disrupted crystal lattices, decreasing in intensity with increasing distance from the point of impact (Stöffler 1965). The structural changes that occur within the crystal lattices of shocked minerals may result in diffusional loss or isotopic resetting (e.g., Nyquist et al. 1979; Bogard 2012; Shih et al. 2014; Petrus et al. 2015; Darling et al. 2016), optical effects (e.g., mechanical twinning, mosaicism; French 1968, 1998; Rubin et al. 1997), or spectral changes (Stöffler 1971; Stöffler and Hornemann 1972; Ostertag 1983; Williams and Jeanloz 1988; Nash and Salisbury 1991; Johnson et al. 2002; Hiroi et al. 2012; Johnson 2012).

The mid-infrared region (~500 to 3000 cm⁻¹, equivalent to 3.5 to 20 μm) of the electromagnetic spectrum is sensitive to both the chemistry and structure of minerals. More specifically, the vibration bands that are diagnostic of mineral composition are present in the Reststrahlen band (RB) region of the spectrum, generally between 6 and 25 μm (Lyon 1963). As such, infrared spectroscopy techniques (e.g., FTIR) are useful for determining changes to crystal lattices as a result of shock metamorphism. Previous studies have focused primarily on mid-infrared spectral characterization of the plagioclase mineral group due to plagioclase being a sensitive indicator of shock level (Ostertag 1983; Nash and Salisbury 1991; Salisbury et al. 1991; Johnson et al. 2002; Wright et al. 2011; Johnson 2012). Johnson et al. (2002) and Johnson (2012) show that Si-O diagnostic bands broaden and have decreased intensities with increasing shock levels up to ~30 GPa in bytownite, albite, and andesine feldspar mineral powders and chips. The Si-O diagnostic bands are the result of stretching of the Si-O bonds within the crystal structure and are situated between ~900 and 1200 cm⁻¹ (~11.1 and 8.3 μm) for plagioclase feldspars (Johnson et al. 2002). Rubin et al. (1997) noted changes in plagioclase crystals in E chondrites: from sharp optical extinction to undulose extinction, isotropicism, transformation to maskelynite, and melting with increasing shock pressures. Furthermore, Johnson et al. (2002) and Johnson (2012) noted a general shift to longer wavelength (lower wave number) of the Christiansen Feature (CF; the point of lowest reflectance in an IR reflectance spectrum situated around 8.1–8.2 μm or 1220–1240 cm⁻¹) with increasing shock levels up to 56 GPa of bytownite and andesine. However, no changes in the CF position of increasingly shocked albite were observed. Johnson et al. (2002) noted that silica tetrahedra (fourfold coordination) within these plagioclases may be transformed to silica octahedra (sixfold coordination) when shocked to levels above 15–20 GPa, resulting in spectral changes between 850 and 400 cm⁻¹ (11.75 and 25 μm).

The spectral characterization of powders with varying physical properties, particularly grain size and composition, is important for comparison to planetary remote sensing data sets due to the fine-grained and compositionally heterogeneous nature of planetary surfaces (Pieters et al. 1993, 2006; Sugihara et al. 2004; Isaacson et al. 2009, 2010). For example, mid-infrared wavelength data have been collected from the surface of the Moon by the Diviner Lunar Radiometer (onboard the Lunar Reconnaissance Orbiter; Paige et al. 2010), and of the surfaces of both the Moon and Mercury from Earth-based telescopic observations (Tyler et al. 1988; Sprague et al. 1994, 2002, 2007; Blewett et al. 1997). The upcoming ESA/JAXA BepiColombo mission (due to arrive at Mercury in 2024) also has a dedicated mid-infrared spectrometer (MERTIS) onboard (Hiesinger et al. 2010).

Although impact modification is currently the dominant surface process on these bodies, its effects upon mid-infrared spectra of surface material are currently not well understood. Although polished thick sections are not truly representative of heavily gardened regolith lunar surface material (e.g., Cooper et al. 2002), they can be used to investigate and quantify changes in the spectrum due to shock modification that may not be apparent from powdered material. Spectral analysis of such samples may, therefore, yield new insights into the possibilities of using mid-infrared spectroscopy to investigate the properties of shocked minerals and clasts (Martin et al. 2016; Morlok et al. 2016). For example, Glocch et al. (2011) and Jaret et al. (2016) studied impactites from the Lunar crater, India; Stephen et al. (2014) and Benedix et al. (2016) mapped Martian meteorites; while Hamilton and Connolly (2012) and Hamilton et al. (2016) investigated the mineralogy and phases present within carbonaceous chondrites using micro-FTIR spectroscopy.

This study investigates the shock history of lunar meteorites Miller Range 090034, 090070, and 090075 (Fig. 1), which were found in 2009 by the Antarctic Search for Meteorites (ANSMET) expedition to the Miller Range mountains (Righter et al. 2010). They are thought to be grouped stones based on their similar compositions and textures and their close proximities to field collection sites (Korotev et al. 2011; Zeigler et al. 2012). Studies of cosmogenic radionuclides ¹⁰Be and ²⁶³Al by Nishiizumi and Caffee (2013) indicate similar Moon–Earth transit times and ejection depths, further supporting the grouping of these rocks. Previous studies
have classified these samples as feldspathic regolith breccias due to the abundance of feldspathic clasts (up to 2 cm long) and low bulk rock iron content (~3.3 wt % FeO) (Korotev et al. 2011; Zeigler et al. 2012; Calzada-Diaz et al. 2016). They are good case study examples of impact modified lunar highlands crust as they contain a range of clasts (largely feldspathic) and impact melt veins, and are dominantly fine-grained, indicating they have experienced multiple impact modification events throughout their history. This paper combines compositional and textural information with mid-infrared studies of each of the samples. Reflectance spectra of individual phases will be used to investigate how properties such as mineral composition and internal structure affect specific band positions.

The spectra presented in this study will be made available in the Berlin Emissivity Database (BED) at the Deutsche Gesellschaft für Luft- und Raumfahrt (DLR) and in the IRIS spectral database at the Westfälische Wilhelms-Universität Münster (http://www.uni-muenster.de/Planetology/en/ifp/ausstattung/iris_spectra_database.html). This is compiled for the interpretation of planetary remote sensing data, such as the upcoming ESA/JAXA BepiColombo mission to Mercury, which has a mid-infrared spectrometer (MERTIS–MERcury Radiometer and Thermal Infrared Spectrometer) on board (Hiesinger et al. 2010). However, the laboratory data collected in this study are not directly applicable to the data collected by remote sensing missions such as MERTIS for a number of reasons. Reflectance spectra

Fig. 1. Backscattered electron (BSE) montages of Miller Range 090034, 090070, and 090075. The dark areas are feldspathic clasts, with lighter regions being impact melt veins. Bright spots are mafic mineral fragments. Boxes represent areas shown in Figs. 6–8. Labeled BSE images of each of the meteorites can be found in Figs. S1–3 in supporting information, indicating regions where spectra and compositional data were obtained. (Color figure can be viewed at wileyonlinelibrary.com.)
from laboratory measurements can be converted to emittance using Kirchhoff’s law (E = 1–R), though the diagnostic mineral bands are stronger in reflectance measurements (and hence, the resulting emittance spectra). The polished samples have also been analyzed in this study, which result in “ideal” mineral spectra, whereas spacecraft measurements are of the powdered planetary surface material. The differences in composition between the lunar samples and Mercurian surface material may also reduce the applicability of the results to MERTIS data, with the anorthitic nature of lunar feldspars being in contrast to the Na- or K-rich feldspars that are likely present on Mercury (Sprague et al. 2009).

METHODS AND MATERIALS

Three lunar meteorite 200 μm polished thick sections were studied: MIL 090034,27, MIL 090070,25, and MIL 090075,21, measuring ~10 × 12 mm, 10 × 10 mm, and 14 × 10 mm, respectively. A backscattered electron (BSE) map of each sample (Fig. 1) was collected using a Phillips FEI XL30 environmental scanning electron microscope-field electron gun (ESEM-FEG) at the University of Manchester. BSE images were collected using beam conditions of 20 keV and a 2 nA beam current.

Major- and minor element concentrations were obtained using a Cameca SX100 electron probe microanalyzer (EPMA) at the University of Manchester. An instrument setup of a 15 keV accelerating voltage, a 20 nA beam current, and spot sizes of 1 μm (focused) and 10 μm (defocused) were used on each of the three samples (1 μm spots for minerals, 10 μm spots for glass and microcrystalline melt phases). Both instruments were calibrated with well-characterized mineral and synthetic standards prior to analysis. Typically, EPMA mineral chemistry 1σ analytical uncertainties by oxide wt% are 0.2 SiO2, 0.02 TiO2, 0.13 Al2O3, 0.03 FeO, 0.03 MgO, 0.09 CaO, 0.02 Na2O, and 0.004 K2O.

Optical microscope-CL color imaging (OM-CL) was acquired using a CITL 8200 mk 3 “cold” CL system coupled to a transmitted light microscope. In addition, we carried out FTIR microspectroscopy analyses with a Perkin-Elmer Spotlight-400 FTIR spectrometer and an adjoining microspectroscopy mapping unit, both at the University of Manchester. During FTIR analysis, mid-infrared reflectance spectra were collected between 4000 cm⁻¹ and 650 cm⁻¹ (~2.5 μm and 15.4 μm) at 4 cm⁻¹ spectral resolution using a cooled mercury-cadmium-telluride (MCT or HgCdTe) detector. The instrument has an aperture size range of 6–1000 μm. Measurements of individual minerals/glasses were made on uncoated polished thick sections with an instrument aperture size of 25 × 25 μm. A total of 32 scans were taken per individual spot measurement, resulting in a signal-to-noise ratio of ~26 (we note that a signal-to-noise ratio of ~28 can be reached with higher numbers of scans, though the time taken to complete a map significantly increases). These scans were coadded to produce a single spectrum of the phase/area targeted (in order to obtain a higher quality averaged spectrum of each area). Maps were collected using varied instrument setups depending on the size of the map and on the area being analyzed. See Table 1 for the instrument setup for each map. The raw spectra for the maps are available in Tables S1, S2, and S3 in supporting information.

The FTIR instrument was calibrated with a polished gold-coated aluminum reflectance standard, and the environmental background measurement (taken using the gold-coated standard) was automatically subtracted from the spectra prior to coaddition. A background calibration spectrum was taken between each set of analyses in order to minimize overall uncertainty related to changes in the thermal background of the surrounding environment. Repeat measurements of the background and a set of standard polished sections allowed for an estimate of precision of the spectra to be made for specific aperture sizes (25, 50, 100, and 1000 μm²). Band positions do not vary by more than 1 cm⁻¹, regardless of aperture size used. Maximum %Reflectance values (R) increase with increasing aperture size, but are highly dependent on the temperature of the environment. The background subtraction corrects for this, but %R values still vary by up to 10% due to differences between the temperatures of the gold standard and the samples. As such, absolute values are not suitable to use for comparison between different samples. Using a band ratio (i.e., absolute values from two fixed points in a given spectrum) negates the effects of variable %R when using a fixed aperture size.

Spectral analysis includes identification of specific spectral features: the position of the Christiansen

Table 1. FTIR map parameters for each of the three maps.

| Map          | Aperture size (μm) | Spectral resolution | Number of scans per measurement |
|--------------|-------------------|---------------------|---------------------------------|
| MIL 34 Map1  | 900 × 900         | 25 × 25             | 4 cm⁻¹                          | 32                              |
| MIL 75 Map1  | 460 × 460         | 20 × 20             | 4 cm⁻¹                          | 32                              |
| MIL 75 Map2  | 460 × 460         | 20 × 20             | 2 cm⁻¹                          | 32                              |
Feature, and the positions and %Reflectance values of the diagnostic mineral bands for each spectrum. These are found using an iterative least-squares peak-fitting algorithm, resulting in an accuracy of 0.1 cm$^{-1}$ and 0.5%R.

Due to the aforementioned variations in %Reflectance values of the spectra, absolute magnitude values are not suitable to use for comparison of spectra between samples. As such, a band ratio was used: 1064/932 cm$^{-1}$. These bands were chosen as the 932 cm$^{-1}$ band is the dominant Si-O stretch peak and is present in all phases (mineral or glass) and the 1064 cm$^{-1}$ band is the point of largest %R variation within the Reststrahlen band region of the spectrum when comparing different phases. As such, this band ratio is the most effective at determining the range of feldspathic phases present in an FTIR reflectance map. Following repeat measurements of the gold-coated aluminum standard (used for background calibration), the instrument uncertainty of the 1064 and 932 cm$^{-1}$ band %R values were calculated. Using these values, the band ratio uncertainty was calculated using a standard method of uncertainty propagation.

To compare FTIR spectra with elemental composition, individually targeted FTIR and EPMA analysis points were collected from the same locations in each thin section. This allows for any compositional differences to be taken into account when comparing spectra. Baseline corrections, such as flattening a spectrum for more accurate peak analysis, were not applied to any of the spectra in this study due to the baselines of the spectra already being flat. All measurements were taken under ambient conditions (i.e., room temperature and standard atmospheric pressure).

RESULTS

Petrography and Geochemistry

The MIL 090034,27 and MIL 090075,21 sections are composed of many small fragments of highly fractured pale gray feldspathic “clast-rich” impact melt breccia (Fig. 1 and see Figs. S1–3). These fragments are generally less than 3 mm in size, separated by a series of dark colored glassy melt veins, ranging in texture from homogenous glass to microcrystalline. In some cases, smaller veinlets cross-cut both the impact melt breccia clasts and the melt veins (Figs. 1 and 2).

MIL 090070,25 differs from the other two samples in that it consists of a single large feldspathic impact melt breccia clast (>10 × 10 mm) with small melt veins that cross-cut it to the left and lower right sides of Fig. 1 (see also Fig. S2).

Most of the impact melt breccia areas are clast-rich composed of larger fragments of plagioclase and smaller (<50 μm) clasts of both unzoned olivine (ranging from Fo55 to Fo75) and pyroxene crystal clasts (Wo43, En43, Fs19,35; Fig. 3). Plagioclase fragments in these impact melt breccias are highly anorthitic (An95,96; Fig. 3). They are extensively fractured (Fig. 2) and generally anhedral in shape. These observations and compositions are in agreement with other studies of these lunar meteorites (Korotev et al. 2011; Zeigler et al. 2012; Calzada-Diaz et al. 2016).

A few (two examples found in MIL 090034 and one example in MIL 090075, Fig. 2a) clasts are igneous lithics, which are crystalline and are more mafic than the impact melt breccias. These clasts are composed of sharp contacting olivine (Fo72–78) and pyroxene (Wo16–23, En32–67, Fs18–45) crystals intergrown with plagioclase (An95,96; Fig. 3).

Olivine and pyroxene Fe/Mn ratios for MIL 090034, 090070, and 090075 are located along the lunar trend line, confirming the lunar origin of these meteorites (Figs. S4 and S5 in supporting information). Furthermore, the major element mineral chemistry of mineral fragments in the impact melt rocks and in the igneous clasts are consistent with these samples deriving from bedrock sources similar to samples from the Apollo highlands ferroan anorthosite (FAN) rock suite (Figs. 3 and 4).

Shock Effects

We collected in situ FTIR spectra for a range of minerals and melt veins in each of the meteorites. The spectral data set has been divided by mineralogy and subdivided by phase to enable a more effective comparison between spectra.

Olivine

Spectral analysis of olivine crystal fragments can be grouped into two main types: normal (i.e., unshocked) and modified spectral patterns (examples are shown in Fig. 5). Normal olivine spectra are only associated with crystal fragments within the feldspathic clast-rich impact melt breccia clasts, whereas modified olivine spectra are displayed by fragments situated within both the feldspathic impact melt breccias (Fig. 2c) and crystalline lithic clasts (Fig. 2a).

Normal olivine spectra display all expected olivine reflectance peaks (Fig. 5), two peaks of highest reflectance situated at 963 cm$^{-1}$ (10.39 μm) and 931 cm$^{-1}$ (10.75 μm), representing Si-O vibration bands in isolated Si-O tetrahedra (Duke and Stephens 1964). These two peaks are separated by an absorption band at 945 cm$^{-1}$ (10.58 μm). Other reflectance peaks are small
and form shoulders on either side of the main peaks at 1016, 1000, 986, 912, 902, and 894 cm\(^{-1}\) (~9.84, 10.01, 10.14, 10.96, 11.09, and 11.19 \(\mu\)m, respectively).

Modified olivine spectra (Fig. 5) lack the shoulder reflectance peaks between 985 and 1015 cm\(^{-1}\) (9.84 and 10.14 \(\mu\)m) that are displayed by normal olivine spectra, and also lack the 962 cm\(^{-1}\) (10.39 \(\mu\)m) peak. An additional, low intensity reflectance band with a peak center of between 945 cm\(^{-1}\) (10.58 \(\mu\)m) and 957 cm\(^{-1}\) (10.45 \(\mu\)m) is present. The highest %Reflectance Si-O vibration band appears in one of two places—either around 903 cm\(^{-1}\) (11.08 \(\mu\)m) or 919 cm\(^{-1}\) (10.88 \(\mu\)m).

Some of the modified olivine spectra also possess a small peak in the vicinity of the Christiansen Feature (CF), centered around 1152 cm\(^{-1}\) (8.68 \(\mu\)m), whereas the expected CF position is around 1110 cm\(^{-1}\) (9.01 \(\mu\)m), making the precise position of the CF difficult to determine for some of the modified olivine spectra. Importantly, the modified olivine spectra display similar features to spectra of normal olivine.

Fig. 2. BSE images of clasts, melt veins, and minerals within MIL 090034, 090070, and 090075. a) Igneous-textured clast. Note the sinuous edges of the olivine (Ol) and pyroxene (Px) crystal fragments within the plagioclase matrix (Plag). b) Typical crystalline anorthite (1) clast-rich impact breccia clast surrounded by polycrystalline impact melt (4). c) A more highly reworked crystalline anorthite (1) clast-bearing impact breccia clast with olivine (Ol) and pyroxene (Px) fragments present. d) Clast-poor impact melt breccia clast surrounded by polycrystalline impact melt (4). Large clasts are highlighted in yellow. (Color figure can be viewed at wileyonlinelibrary.com.)
some of these modified olivine spectra may be due to orientation effects and not due to an alteration effect (e.g., shock). However, with an individual feldspathic impact melt breccia clast containing multiple olivine clasts, the individual crystal fragments display either all normal spectra or all modified spectra, indicating that random orientation of the olivine grains is not a major factor in these areas.

**Pyroxene**

The pyroxene crystal fragments display a wide range of spectra with highly variable %Reflectance values and peak positions (Fig. 5). This is likely due to variations in major element composition (Hamilton 2000, 2003), but could also be due to variations in shock level experienced. Pigeonite is the most common pyroxene in MIL 090034, 090070, and 090075 (Fig. 3a), displaying spectra with a dominant reflectance peak at 1088 cm$^{-1}$ (9.19 µm) (also observed by Hamilton 2000), and with smaller reflectance peaks at $\sim$1020 (shoulder), 955, 935, 892, and 720 cm$^{-1}$ (9.80, 10.47, 10.70, 11.21, and 13.89 µm). However, there are too few pyroxene grains in these samples to group the spectra based on compositional variations or shock states.

**Plagioclase**

Plagioclase within these samples are highly calcic (An$_{94-98}$; Fig. 3c, Tables 2–5) and display a wide range of shock states ranging from crystalline anorthitic plagioclase, to partially shock-modified plagioclases, and maskelynite; each of which exhibit distinct FTIR spectra (Figs. 6–8).

Type (1): Crystalline anorthite

The main “clastic” component of the impact melt breccia clasts found throughout each of the samples is crystalline anorthite (e.g., Fig. 2b). The spectra of this phase display a prominent reflectance band at 932 cm$^{-1}$ (10.75 µm) (similar to 940 cm$^{-1}$ as reported by Johnson et al. 2002) and other major bands situated at 1147, 1103, 1022, 987 (shoulder), 755, 725, 681, and 668 cm$^{-1}$ (8.72, 9.07, 9.78, 10.13 [shoulder], 13.24, 13.79, 14.68, and 14.98 µm, respectively) (Figs. 6c, 7c, and 8c). Maximum reflectance values of the main Si-O stretch peak at 932 cm$^{-1}$ (or 10.75 µm) vary between $\sim$40 and 70%R. CF position averages around 1224 ± 10.5 cm$^{-1}$ (8.17 ± 0.07 µm, 1σ uncertainty). The uncertainty in the CF positions is likely due to the many fractures present within the samples that induce noise into the spectra, resulting in the minimum point in the spectrum being offset from the true CF position (while all efforts to avoid fractures has been made, the samples are too heavily fractured to avoid cracks entirely). Reflected
light images and EMPA data indicate that it is not the result of changes of composition or inclusion of more mafic minerals (e.g., olivine or pyroxene) within the areas studied.

Type (2): Partially shock-modified anorthite

A small portion of spectra are representative of plagioclase, but are missing some of the crucial reflectance bands indicative of crystalline plagioclase, illustrating the effects of shock modification. They display reduced %R values of the Si-O stretch band by up to 20% and have barely discernible peaks at 1147 and 1103 cm\(^{-1}\) (8.72 and 9.07 \(\mu\)m), but a higher %R value at 1064 cm\(^{-1}\). CF positions remain the same as for the type (1) crystalline plagioclase spectra, and mineral chemistry data also show no compositional differences between these spectra and crystalline anorthite. Therefore, they have been grouped as partially shock-modified anorthite.

**Table 2. Average compositions of plagioclase, olivine, and pyroxene in MIL 090034, MIL 090070 and MIL 090075.**

| Section # | Plagioclase | Olivine | Pyroxene |
|-----------|-------------|---------|----------|
|           | MIL 090034,27 | MIL 090070 | MIL 090075,21 | MIL 090034,27 | MIL 090070 | MIL 090075,21 | MIL 090034,27 | MIL 090070 | MIL 090075,21 |
| SiO\(_2\)  | 43.93       | 43.68   | 44.06    | 36.34       | 36.48       | 36.65       | 51.70       | 53.47       | 51.83       |
| TiO\(_2\)  | B.D.        | B.D.    | B.D.     | 0.01        | B.D.        | 0.02        | 0.83        | 0.20        | 0.50        |
| Al\(_2\)O\(_3\) | 35.10      | 35.08   | 35.25    | 0.16        | 0.09        | 0.04        | 1.64        | 1.32        | 0.95        |
| FeO       | 0.32        | 0.26    | 0.31     | 32.23       | 31.66       | 32.11       | 17.83       | 14.11       | 21.73       |
| MgO       | 0.19        | 0.13    | 0.18     | 30.01       | 31.48       | 30.99       | 19.62       | 25.43       | 17.52       |
| CaO       | 19.30       | 19.38   | 19.25    | 0.24        | 0.20        | 0.21        | 7.03        | 3.90        | 7.04        |
| Na\(_2\)O | 0.40        | 0.39    | 0.41     | B.D.        | B.D.        | B.D.        | 0.01        | B.D.        | B.D.        |
| K\(_2\)O  | 0.02        | 0.02    | 0.03     | B.D.        | B.D.        | B.D.        | B.D.        | B.D.        | B.D.        |
| Sum       | 99.3        | 98.94   | 99.49    | 98.99       | 99.91       | 100.02      | 98.66       | 98.43       | 99.57       |
| An#       | 96.28       | 96.41   | 96.13    | 62.28       | 63.78       | 63.16       | 65.57       | 76.24       | 59.13       |
| Mg#       | 47.68       | 42.43   | 44.74    | 62.28       | 63.78       | 63.16       | 65.57       | 76.24       | 59.13       |
| Wo#       | 14.77       | 7.78    | 14.71    | 14.77       | 7.78        | 14.71       | 14.77       | 7.78        | 14.71       |
| En#       | 56.20       | 70.32   | 50.20    | 56.20       | 70.32       | 50.20       | 56.20       | 70.32       | 50.20       |
| Fe#       | 29.03       | 21.90   | 35.09    | 29.03       | 21.90       | 35.09       | 29.03       | 21.90       | 35.09       |

B.D., measurements that are below the detection limit of the instrument.
Table 3. Chemical compositions of three feldspathic phases found in MIL 090034 area (shown in Fig. 6d) for points coaligned with FTIR spectra shown in Fig. 6c. Full FTIR spectra for these phases are provided in Table S1.

| Compositions                  | Crystalline plagioclase (phase 1 and 2) | Maskelynite (Phase 3) | Devitrified feldspathic glass (Phase 5) |
|-------------------------------|----------------------------------------|-----------------------|----------------------------------------|
| SiO2                          | 43.76                                  | 43.61                 | 44.76                                  |
| TiO2                          | B.D.                                   | B.D.                  | 0.12                                   |
| Al2O3                         | 36.06                                  | 36.25                 | 32.38                                  |
| FeO                           | 0.22                                   | 0.13                  | 2.40                                   |
| MgO                           | 0.08                                   | 0.03                  | 2.23                                   |
| CaO                           | 19.71                                  | 19.61                 | 18.20                                  |
| Na2O                          | 0.34                                   | 0.35                  | 0.36                                   |
| K2O                           | 0.01                                   | 0.02                  | 0.04                                   |
| Sum                           | 100.2                                  | 100.0                 | 100.5                                  |
| An#                           | 96.9                                   | 96.8                  | 96.3                                   |
| Mg#                           | 38.6                                   | 31.4                  | 62.3                                   |
| CF position (cm⁻¹)            | 1222                                   | 1218                  | 1208                                   |
| 1064/932 cm⁻¹ band ratio      | 0.17                                   | 0.52                  | 0.99                                   |

B.D., measurements that are below the detection limit of the instrument.

Type (3): Maskelynite

Maskelynite spectra represent plagioclase that has undergone shock deformation (>~25 GPa; Rubin et al. 1997), but retains the same chemical composition as the type (1) crystalline and (2) partially shocked plagioclase (see Tables 3–5). Maskelynite phases have spectra with a reduced number of reflectance bands compared to the crystalline anorthite spectra (Figs. 6 and 7). The main Si-O stretch at 931 cm⁻¹ (10.75 µm) is present, with a steadily increasing %R trend from 840 cm⁻¹ to 931 cm⁻¹ (11.90 µm–10.75 µm). Maskelynite spectra also have reduced Si-O reflectance band intensities compared to crystalline anorthite (between ~25 and 40% R). The CF position averages around 1226 ± 10.0 cm⁻¹ (8.16 ± 0.06 µm) with the large uncertainty being due to fractures in the sample. See Fig. 7.a for a backscattered electron image with maskelynite present.

Glassy Components

There are three other types of feldspathic glass-rich phases/lithologies found in the samples that help to shed light on the range of impact processes witnessed by the meteorites.

Type (4) Polycrystalline Impact Melt

All polished sections (Fig. 1) and the parent hand specimen-sized meteorite samples (Korotev 2016) are cross-cut by millimeter-sized vein networks infilled with glassy feldspathic melt (see also the “dark melt” discussed in the section studied by Calzada-Díaz et al. 2016). These melt vein networks are heterogeneous, having patchy mafic and felsic regions (see Figs. 7a and 8a), the average composition of which is enriched in FeO and MgO by ~2 wt% relative to the plagioclase phases (1), (2), and (3) (Tables 3–5). This melt material appears to surround and encase the large clast-rich impact melt breccias. We term this material “polycrystalline impact melt” reflecting the intermixed glassy and very fine crystalline material found in the vein networks. The spectral characteristics of this material are similar to (3) maskelynite spectra (Figs. 6c, 7c, and 8c) with respect to the increasing %R trend between 840 cm⁻¹ and the Si-O stretch band at 931 cm⁻¹ (11.90 µm–10.75 µm). They also have similar maximum %R values (25–40%R) and full-width half-maximum (FWHM) values (220 cm⁻¹ for [4] polycrystalline impact melt, and 240 cm⁻¹ for [3] maskelynite) of the main Si-O stretch band at 931 cm⁻¹. These melt vein regions are compositionally similar to the type (5) devitrified feldspathic glass phases (major element totals are within 1.5%—see Tables 4 and 5) with higher proportions of FeO and MgO, and lower bulk An# and higher Mg# values than (1) crystalline plagioclase and (3) maskelynite phases.

Type (5) Devitrified Feldspathic Glass

Two of the three meteorites, MIL 090034 and MIL 090075, contain feldspathic phases of similar composition to (4) polycrystalline impact melt material, but that have different mid-IR spectral profiles. These phases are found as localized pockets within the polycrystalline impact melt veins (type [4]), but have a different texture and appear to be the result of devitrification of melt vein material (see Figs. 7a and 8a). As such, these phases have been termed “devitrified feldspathic glasses.” They consist of a broad peak between 870 and 1050 cm⁻¹ (~9.52 and 11.49 µm) with similar %R values as (3) maskelynite and there are no defining peaks within this broad region that represent the Si-O stretch reflectance band. The average CF position is at a longer wavelength than the other spectral types: 1207 ± 11.3 cm⁻¹ (8.29 ± 0.08 µm).

Type (6) Homogenous Feldspathic Glass

Some homogeneous melt veinlets are found cross-cutting existing clasts in each of the samples (Figs. 7a and 8a, Figs. S1–3). They are compositionally similar to the average composition of the (4) polycrystalline impact melt and (5) devitrified feldspathic glass phases (all major oxides of these phases except Al₂O₃ are
within 1.5 wt%), and have similar spectral profiles to (3) maskelynite and (4) polycrystalline impact melt areas (an increasing %R trend between 840 cm\(^{-1}\) and 931 cm\(^{-1}\), Fig. 8c).

**FTIR Maps and CL Images**

Full-spectral data cube maps of specific areas of the samples have been collected for visual comparison between different spectral types within a small area (raw data present in Tables S1, 2, and 3). Figure 6 shows an example of an FTIR map that has been centered on a region of MIL 090034 (area indicated on Fig. 1), containing a clast-rich impact melt breccia (1) crystalline anorthite (lower portion of map) and a (4) polycrystalline impact melt area (mid-section of map) bearing (3) maskelynite with minor olivine and pyroxene mineral phases. There is also a pocket of (5) devitrified feldspathic glass (upper region) that appears to be in sharp contact with the (4) polycrystalline impact melt. Although each pixel of each FTIR map contains the entire mid-infrared spectrum, maps

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**Table 4. Compositions of four feldspathic phases found in MIL 090075, corresponding to FTIR spectra shown in Fig. 7c. Full FTIR spectra for these phases are provided in Table S2.**

|                | Crystalline plagioclase (Phase 1 and 2) | Maskelynite (Phase 3) | Polycrystalline impact melt (Phase 4) | Devitrified feldspathic glass (Phase 5) |
|----------------|---------------------------------------|-----------------------|---------------------------------------|----------------------------------------|
| SiO\(_2\)      | 43.59                                 | 43.65                 | 44.19                                 | 45.19                                  |
| TiO\(_2\)      | B.D.                                 | B.D.                 | 0.13                                 | 0.15                                  |
| Al\(_2\)O\(_3\) | 36.19                                 | 36.22                 | 31.14                                 | 29.65                                  |
| FeO            | 0.08                                 | 0.09                 | 2.76                                 | 2.55                                  |
| MgO            | 0.06                                 | 0.05                 | 2.43                                 | 2.48                                  |
| CaO            | 19.70                                 | 19.67                 | 17.75                                 | 18.82                                  |
| Na\(_2\)O      | 0.23                                 | 0.22                 | 0.36                                 | 0.41                                  |
| K\(_2\)O       | B.D.                                 | B.D.                 | 0.03                                 | 0.04                                  |
| Sum            | 99.85                                 | 99.89                 | 98.79                                 | 99.28                                  |
| An\#           | 97.9                                 | 98.06                 | 96.3                                 | 96.0                                  |
| Mg\#           | 54.4                                 | 46.69                 | 61.1                                 | 63.5                                  |
| CF position (cm\(^{-1}\)) | 1220                         | 1222                 | 1212                                 | 1196                                  |
| 1064/932 cm\(^{-1}\) band ratio | 0.17                         | 0.59                 | 0.54                                 | 0.87                                  |

B.D., measurements that are below the detection limit of the instrument.

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**Table 5. Compositions of five feldspathic phases found in MIL 090075, corresponding to spectra in Fig. 8c. Full FTIR spectra for these phases are provided in Table S3.**

|                | Crystalline plagioclase (Phase 1 and 2) | Maskelynite (Phase 3) | Polycrystalline impact melt (Phase 4) | Devitrified feldspathic glass (Phase 5) | Homogeneous melt (Phase 6) |
|----------------|---------------------------------------|-----------------------|---------------------------------------|----------------------------------------|---------------------------|
| SiO\(_2\)      | 44.33                                 | 44.32                 | 45.45                                 | 44.64                                  | 44.41                     |
| TiO\(_2\)      | B.D.                                 | B.D.                 | 0.15                                 | 0.10                                  | 0.13                       |
| Al\(_2\)O\(_3\) | 35.72                                 | 35.51                 | 29.99                                 | 32.52                                  | 32.36                     |
| FeO            | 0.18                                 | 0.22                 | 3.20                                 | 2.32                                  | 2.31                       |
| MgO            | 0.11                                 | 0.10                 | 2.98                                 | 2.02                                  | 1.88                       |
| CaO            | 19.33                                 | 19.34                 | 17.38                                 | 18.49                                  | 18.04                     |
| Na\(_2\)O      | 0.44                                 | 0.45                 | 0.36                                 | 0.40                                  | 0.38                       |
| K\(_2\)O       | B.D.                                 | B.D.                 | 0.02                                 | 0.02                                  | 0.03                       |
| Sum            | 100.10                               | 99.93                 | 99.54                                 | 100.50                                 | 99.54                     |
| An\#           | 96.1                                 | 96.0                  | 96.2                                 | 96.1                                   | 96.2                       |
| Mg\#           | 50.8                                 | 45.9                  | 62.4                                 | 60.9                                   | 59.1                       |
| CF position (cm\(^{-1}\)) | 1222                         | 1224                 | 1206                                 | 1196                                  | 1200                      |
| 1064/932 cm\(^{-1}\) band ratio | 0.16                         | 0.48                 | 0.44                                 | 0.85                                  | 0.62                       |

B.D., measurements that are below the detection limit of the instrument.
showing specific band positions have been chosen for best visual comparison (in the case of Figs. 6 and 7, the maps show the 1064/932 cm\(^{-1}\) band ratio). Color cathodoluminescence (CL) images of these regions have also been collected and clearly distinguish the state of different phases present (Figs. 6 and 7). The components can also be distinguished in clearer detail than in the BSE images, with the crystalline plagioclase phases displaying a range of bright oranges and greens, typical of fresh unshocked plagioclase (Gotze et al. 1999). Maskelynite generally appears in CL as a dark blue color, whereas the devitrified feldspathic glass region displays a vivid red color, reflecting its higher FeO abundance (Gotze et al. 1999). The polycrystalline impact melt vein material and mafic crystal fragments are black in these CL images, providing a clear distinction between the (4) impact melt vein and (3) maskelynite phases (in contrast to their highly similar FTIR spectra).

A second FTIR map (also showing the 1064/932 cm\(^{-1}\) band ratio) has been collected in a small region of MIL 090075 (area indicated in Fig. 1) that includes all
four feldspathic phases in close proximity (Fig. 7). The BSE image of this region shows a large anorthite crystal that grades from (1) crystalline anorthite to (3) maskelynite, in contact with (4) polycrystalline impact melt vein and (5) devitrified feldspathic glass material. The FTIR map shows the change from the (1) crystalline anorthite to (3) maskelynite in the large plagioclase crystal, and can clearly distinguish between these phases and (5) devitrified feldspathic glass material. However, it is not possible to distinguish between (3) maskelynite and (4) polycrystalline impact melt vein material using this band ratio approach alone. Color CL images clearly show the boundaries of the (1) crystalline plagioclase, (4) polycrystalline impact melt, and (5) devitrified feldspathic glass. However, the transition between (1) crystalline plagioclase and (3) maskelynite within the large plagioclase crystal is not clear.

**DISCUSSION**

By combining FTIR spectra and maps, CL-imaging, and mineral major element chemistry, we are able to understand the effects of shock on the texture and composition of individual phases, along with identifying subdivisions of spectral types for compositionally similar anorthite ($An_{94-98}$) and olivine ($Fo_{50-55}$) phases.
This allows us to determine the shock history and formation of the lunar meteorites studied and by extension, further investigate the formation and evolution of the lunar crust.

**Lunar Crustal Heritage**

Miller Range 090034, 090070, and 090075 contain mineral phases similar to a range of lunar highland crustal protoliths, including norites, gabbros, and anorthosites (Figs. 3 and 4). The impact melt breccia clasts are dominantly feldspathic in composition, dominated by a crystalline to shocked anorthite mineral population. This indicates that the precursor rock type was anorthositic in nature. When mafic mineral Mg# is compared with plagioclase An#, the material sampled is dominantly within the range of pristine rocks from the Apollo ferroan anorthosite suite (Fig. 4). This is consistent with what was also observed by Liu et al. (2011) and Calzada-Diaz et al. (2016) in other subsplits of these samples. However, when comparing the olivine compositions within the lithic crystalline clasts (e.g., Fig. 2a) and impact melt breccia clasts (e.g., Fig. 2c) in MIL 090034 and 090075, there is a compositional difference, with the lithic clast olivine being ~10% more forsteritic. As such, this clast falls in the magnesian anorthositic “compositional gap” between the FAN suite and Mg-suite identified in many other feldspathic lunar meteorites (Stöffler et al. 2006; Gross et al. 2014).
Shock History Recorded by Miller Range Meteorites

Plagioclase is the most abundant and compositionally constant mineral (An# 94-98) present throughout each sample of study. It is a good indicator of shock level due to the range of optical effects displayed at different shock pressures (Rubin et al. 1997), and when analyzed using FTIR spectroscopy, shocked feldspathic phases display different spectral features compared to unshocked crystalline feldspars (e.g., Figs. 6c, 7c, and 8c). By contrast, olivine and pyroxene are not as effective as shock indicators as plagioclase is, due to these phases being more resistant to shock alteration (Rubin et al. 1997). At least three pyroxene spectral types were identified in this study (Fig. 5b), but due to their low abundance (<15 crystal fragments) and compositional heterogeneity, it is impossible to identify spectral changes due solely to shock and not composition. Two spectral types of olivine were identified in this study (Fig. 5a), with one being a more highly shocked phase (due to the compositional homogeneity is this phase). However, it is currently not possible to determine the shock pressure that results in this spectral change without comparison to optical features.

Along with composition and shock, crystal size and orientation are important contributing factors to mid-IR spectra of crystalline phases. The orientation effects of anorthite can be taken into account from previous studies (Reynard 1991) and from calibration standards at the University of Manchester (e.g., Miyake Jima anorthite crystals, chosen due to their compositional similarity to lunar anorthite; Brydges et al. 2015). Crystal size can alter mid-IR spectra if the aperture size is larger than the crystal or phase being analyzed, resulting in an average spectrum representative of all materials within that area. For example, in this study, (4) polycrystalline impact melt material is a mixture of feldspathic and mafic phases at the micron and submicron scales, whereas the smallest aperture size used is 20 μm, resulting in an average spectrum of the phases present.

To investigate and try to calibrate the shock pressure regime for each of the feldspar component spectral types (i.e., (1) crystalline anorthite, (2) shocked anorthite, (3) maskelynite, (4) polycrystalline impact melt, and (5) devitrified feldspathic glass), spectral patterns were compared to the Reflectance Laboratory spectral database (see RELAB 2016) and flat-plate shock experiments of terrestrial feldspars (Johnson et al. 2002; Johnson 2012). The NASA Reflectance Experiment Laboratory (RELAB) database contains emission spectra of powdered samples, of which the band positions of coarse (>250 μm) anorthite powder are comparable for low-shocked phases (e.g., the type (1) crystalline anorthite). Johnson (2012) used the Flat Plate Accelerator at the Johnson Space Center to induce planar shock waves into terrestrial Stillwater anorthosite targets (note that these are not pure anorthosites but contain a few % orthopyroxene, clinopyroxene, and quartz, depending on where the samples originated). The speed and size of the projectile were used to calculate the shock levels induced into the anorthosite target, and the resulting emission spectra of the shocked powders and chips were analyzed. Johnson (2012) demonstrated how various band ratio values can be used to estimate shock pressures experienced by anorthositic phases. However, many of these ratios are not suitable for this study due to detection limits of instrumentation used or due to large uncertainties associated with the ratios. Therefore, we have used a new band ratio to estimate the range of shock pressures experienced by the phases in the meteorites of this study: 1064/932 cm⁻¹ (Figs. 6c, 7c, and 8c).

This band ratio has been applied to FTIR spectral maps of specific regions of MIL 090034 and 090075 to create images of these areas that distinguish between the phases of different shock levels (Figs. 6d, 7d, and 8d). Compared to the 932 cm⁻¹ (10.75 μm) Si-O reflectance band position, the 1064 cm⁻¹ (9.40 μm) feature is an area of low reflectance in crystalline anorthite spectra, intermediate reflectance in maskelynite and impact melt vein spectra, and high reflectance devitrified feldspathic glass spectra (Figs. 6c, 7c, and 8c). As such, the resulting band ratio maps show each of the spectral types as different colors, allowing for easy distinction between the types of anorthitic phases. Spectra with maximum %R values <18% are the result of fractures within the samples and, as they are not representative of a mineral or phase, have been removed from the spectral maps accordingly (denoted by black pixels).

1. Crystalline anorthite spectra represent anorthite that has been subject to low shock levels. Comparing their spectra with previous plagioclase IR studies (Rubin et al. 1997; Johnson et al. 2002; Milam et al. 2004; Donaldson Hanna et al. 2012b, 2014) suggests this spectral type, with dominant features around 1103 and 1147 cm⁻¹ (8.72 and 9.07 μm), represents plagioclase that has been subject to shock pressures of <25 GPa, and probably <15 GPa. These spectra have an average 1064/932 cm⁻¹ band ratio value of 0.29 ± 0.14 (2σ), the lowest ratio value of all feldspathic material in these samples.

2. Some of the crystalline anorthite spectra show lower %R values of the Si-O stretch reflectance band at 932 cm⁻¹ (10.75 μm), it is likely that the decrease in total %R in this region is due to increasing shock
levels: between 15 and 25 GPa. This is consistent with changes in CL measurements of plagioclase that has been shocked to levels greater than 20 GPa (shifts in band positions and decreased intensities, Kayama et al. 2009) and optical images that show partial isotropism of plagioclase shocked to levels >15 GPa.

3. Maskelynite spectra represent highly shocked plagioclase. These grains, with anorthite-like compositions, have experienced pressures between ~25 and ~45 GPa (Stöffler et al. 1991; Schmitt et al. 1994; Schmitt and Stöffler 1995; Rubin et al. 1997). The spectral pattern of maskelynite was displayed by experimentally shocked grains that had experienced higher than ~25.5 GPa by Johnson et al. (2002). The CF positions of (1) crystalline anorthite, (2) shocked anorthite, and (3) maskelynite do not vary, indicating that CF position is unaffected by shock level (confirming work by Nash and Salisbury 1991). Maskelynite spectra have a 1064/932 cm\(^{-1}\) band ratio average of 0.60 ± 0.09 (2σ).

4. The polycrystalline impact melt veins represent an average bulk composition of the meteorites (this is in agreement with bulk measurements made by Zeigler et al. [2012] and Calzada-Díaz et al. [2016]). As this material represents the matrix and is found between and within the feldspathic clasts, we interpret that this phase is the primary consolidator of the Miller Range meteorites. The single Si-O stretch peak is representative of short-range Si-O bonds, typical of rapidly cooled melt material (Best 2002). These spectra are similar to (3) maskelynite spectra with respect to reflectance band positions and overall shape, 1064/932 cm\(^{-1}\) band ratio values, and total %Reflectance values, even though their textures are highly different when observed in the BSE images. It is important to note the absence of the broad peak (usually situated between 870 and 1050 cm\(^{-1}\), equivalent to ~9.52 and 11.49 μm) as this indicates that no preservation of 6-coordination Si-O is present in this impact melt vein material (unlike the devitrified feldspathic glasses). Therefore, either this material has been shocked to lower pressures than the (5) devitrified feldspathic glasses, or it has been shocked to similar pressures but their mode of formation prevents preservation of this more highly shocked 6-coordination Si-O.

5. Devitrified feldspathic glass possess spectra with a broad peak in contrast with the sharp ~931 cm\(^{-1}\) peak of (4) polycrystalline impact melt. The compositional similarity of the (5) devitrified feldspathic glass phases compared to the (4) polycrystalline impact melt phases, along with both phases being found in between clasts and not within clasts, indicates similar formation conditions. The spectral differences observed, therefore, represent structural heterogeneities, with (5) devitrified feldspathic glass being a more highly shocked phase of (4) polycrystalline impact melt. The broad peak natures of these spectra could be indicative of Si-O being preserved in both 4- and 6-coordination, where 4-coordination Si-O tetrahedra are transformed by the high shock pressures to 6-coordination Si-O octahedra (Haines et al. 2001). If this is the case, (5) devitrified feldspathic glass phases represent material that was shocked to pressures >45 GPa (Stöffler et al. 1991; Haines et al. 2001). The devitrified feldspathic glass spectral type is divided into two subgroups: those with highest %Reflectance values located near to 1002 cm\(^{-1}\) (9.98 μm), and those with their highest %Reflectance values at 936 cm\(^{-1}\) (10.68 μm). This could be due to different proportions of 6- and 4-coordination Si-O, respectively, being preserved in different regions of the devitrified feldspathic glass phases. Devitrified feldspathic glass spectra are similar in character to the feldspathic fusion-formed glasses in the study by Ostertag (1983), but do not match any of the shocked chip or powder spectra analyzed by Johnson et al. (2002) and Johnson (2012), likely due to differences in analytical or shock-induction methods. The CF positions of (4) polycrystalline impact melt and (5) devitrified feldspathic glass are at longer wavelengths than (1) crystalline anorthite, (2) shocked anorthite, and (3) maskelynite due to an enhancement of FeO and MgO by 0.5 to 3%. Given that CF position does not change between (1) crystalline anorthite, (2) shocked anorthite, and (3) maskelynite, it is apparent that CF position is not affected by changes in shock level experienced, but by compositional heterogeneities alone. With a value of 0.92 ± 0.14 (2σ), devitrified feldspathic glass spectra have the highest 1064/932 cm\(^{-1}\) band ratio average.

6. Homogeneous feldspathic glass phases are small regions or thin veinlets of melt material that show no variation in composition or texture. Their spectra are similar to (3) maskelynite and (4) polycrystalline impact melt, indicating a similar internal structure (i.e., very short-order Si-O bonding with no large-scale structure present). Veins of this material appear to cross-cut all pre-existing features, suggesting they are the result of late-stage processes. The 1064/932 cm\(^{-1}\) band ratio results in values that are distinct for each spectral type of feldspathic phase and glassy material (Fig. 9). A k-means clustering
A k-means clustering algorithm has been applied to each of the infrared maps in order to classify the band ratio value of each pixel into one of three groups. The groups represent the spectral types, and therefore the ranges of maximum shock levels experienced that can be distinguished by the band ratio in polished lunar samples: up to 25 GPa for (1) crystalline anorthite and (2) shocked anorthite; 25–45 GPa for (3) maskelynite; and >45 GPa for (5) devitrified feldspathic glass. However, distinguishing between higher shock types (3) maskelynite, (4) polycrystalline impact melt, and (6) homogeneous feldspathic glass is not possible using the 1064/932 cm$^{-1}$ band ratio due to the spectral profiles of these phases, and therefore their band ratio values, being too similar.

Figure 9 shows the distribution of the three groups graphically and the power-law trend that exists between the band ratio values and the 932 cm$^{-1}$/C0$^1$%R value. The average 1064/932 cm$^{-1}$ band ratio value for each k-means “group” is 0.28 ± 0.11 for (1) crystalline anorthite, 0.57 ± 0.19 for (3) maskelynite, and 0.92 ± 0.15 for (5) devitrified feldspathic glass; the 2σ uncertainties indicate the groups are well constrained with little overlap between groups. The divisions between the three groups identified by the k-means algorithm (as shown in Fig. 9 by the vertical black lines) are 0.42 for the transition between plagioclase (1) and maskelynite (3), and 0.75 for the maskelynite (3) to devitrified feldspathic glass (5) transition.

In polished lunar samples, this method can be used to estimate the maximum shock values experienced by any feldspathic phase and classify the mineral type or phase present. This technique can easily be applied to many individual spectra in a short period of time to allow for rapid shock estimates to be made without having to identify each of the spectral types individually. Also, it can be applied to spectral maps (as in Figs. 6d, 7d and 8d) to help qualitatively visualize the changes of shock in any given area of a sample.

The results between samples can also be compared and contrasted, removing uncertainties that rely on manual classification (such as optical microscope studies of shocked phases), and providing a standard method of feldspathic phase identification and shock estimation for lunar samples. This technique has yet to be applied to mineral or rock powders, but if this trend is observed in powdered samples, it may be possible to use this ratio in the future to investigate the shock history using planetary remote sensing studies of plagioclase-dominated regoliths (e.g., mapping exposures of “pure” lunar anorthosite) (Ohtake et al. 2009; Yamamoto et al. 2012; Donaldson Hanna et al. 2014), or in situ on the lunar surface from a lander or rover platform using IR spectroscopy investigations of individual anorthositic rocks. We note that the Diviner Lunar Radiometer data set is currently analyzing the lunar surface in mid-IR wavelengths, but possesses just
one band within the 7–15 μm region, making it impossible to currently apply the 1064/932 cm⁻¹ shock indicator ratio to determine the nature of feldspathic phases at the lunar surface.

It has to be taken into account that spectra from planetary surfaces come from fine-grained, porous material under varying atmospheric pressures and surface temperatures. These different conditions can influence band shapes, positions, and intensities (e.g., Cooper et al. 2002; Donaldson Hanna et al. 2012a.; Donaldson Hanna 2017). The investigation of such factors will be part of future studies.

Crustal Affiliation, Evolution, and Shock History of the Meteorites

The MIL 090034, MIL 090070, and MIL 090075 bulk rock samples have low concentrations of KREEP (0.28–1.11 ppm Th, average of all three samples is 0.53 ppm Th: Korotev and Zeigler 2014, Calzada-Diaz et al. 2016) suggesting that the samples investigated in this study were formed of lithologies not associated with the nearside KREEP-rich Procellarum KREEP Terrane (where regoliths typically have >2 ppm Th; see Fig. 1 of Gross and Joy 2017). Likewise the samples are not from a region bearing alkali-suite, KREEP basalts, incompatible trace element-rich impact melts, or mare basalts as these lithologies are not petrographically or mineralogically observed in the samples. Calzada-Diaz et al. (2016) investigated potential launch sites of MIL 090070, finding that some areas of the Feldspathic Highland Terrane, on the lunar farside, and some outer regions of the FHT near Orientale basin and the south central nearside highlands are possible areas of origin for the meteorite group.

Crustal Precursor Rocks

The material that dominates the MIL samples was predominantly derived from a ferroan anorthositic parent rock. Such ferroan anorthosite lithologies are generally thought to represent primary crust, formed during differentiation of a global Lunar Magma Ocean and floatation of anorthite crystals prior to ~4.36 Ga (Wood et al. 1970; Snyder et al. 1992; Shearer et al. 2006; Elkins-Tanton et al. 2011; Borg et al. 2015; Pernet-Fisher and Joy 2016). Nyquist et al. (2016) analyzed plagioclase formation ages in MIL 090034 and 090070 using the Sm/Nd isotopes chronometer, which yielded a formation age of ~4.5–4.4 Ga, indicative of such early crustal formation.

Samples of relatively unshocked ferroan anorthositic precursor rocks are represented in the MIL sample by the rare lithic clasts (Fig. 2) and the (1) crystalline anorthite mineral component found as clasts in the feldspathic impact breccia clasts. These are relatively unshocked, recording shock pressures of <25 GPa (Fig. 9). Similar unshocked plagioclase from anorthositic crustal precursors has also been recorded in the lunar highlands from orbit in the inner rings of impact basins (Yamamoto et al. 2012; Check et al. 2013; Donaldson Hanna et al. 2014).

Shock Modification History

Lead isotope studies by Bouvier et al. (2013) and argon isotope age studies by Park et al. (2013), Nyquist et al. (2016), and Calzada-Diaz et al. (2016) suggest Miller Range 090034, 090070, and 090075 were significantly isotopically reset at ~3.9 Ga, possibly recording the time of crustal excavation in a basin or impact crater formation event. The timing of this event is consistent with the estimated ages of impact basins that formed at the end of the basin-forming epoch (Wilhelms 1987; Stöffler et al. 2006), although here we cannot relate the ages of the MIL stones to a specific basin or impact cratering event, and the compositional paucity of KREEP, precludes a link to Imbrium.

Such a significant crustal excavation episode likely constructed the impact melt breccia clasts (Fig. 2b and 2c) and caused modification of feldspathic phases from pristine anorthite (1) to shocked variations between type (2) to (3) (Figs 6–8). Such shock effects must have been heterogeneous on the micron to cm scale, resulting in higher shock pressures to be experienced in some areas of the parent rock as represented by phases (2)–(3).

The polycrystalline impact melt (4) and devitrified glass (5) represent shock pressures of >45 GPa that caused melting of both feldspathic and mafic phases. The phases are only found in between feldspathic clasts (and never within a clast) (see also the “dark melt” of Calzada-Diaz et al. 2016). This suggests that either (1) the propagating shock wave was focused into pre-existing zones of weakness causing frictional in situ melting of minerals in these regions, or (2) after formation the impact melt breccia material (i.e., Fig. 2b, 2c, and 2d) were mixed into a different reservoir of finer grained “dark colored” feldspathic impact melt (represented by both types (4) and (5)). It is hard to untangle these interpretations given the available compositional evidence.

Recent Shock History

Since the formation of the parent rock, further impact argon isotopic resetting occurred until around 3 Ga (Park et al. 2013; Calzada-Diaz et al. 2016; Nyquist et al. 2016). We suggest that this most recent phase of impact shock resulted in the formation of (6) homogeneous glassy melt material that cross-cuts pre-
existing feldspathic phases and clasts. Its chemical composition, which is similar to the “dark melt” regions (types (4) and (5)) (Table 5), supports a model of in situ (i.e., pseudotachylitic) frictional melting of the parent rock. There appears to be no correlation between the locations of (6) homogeneous melt and other shocked phases (such as (3) maskelynite) suggesting that impact modification while the sample was in the upper regolith layers resulted only in highly localized areas of shock modification.

Ejection from the Moon

Since its formation, the parent rock sat at shallow depths within the regolith (10–60 g/cm$^2$; Nishizumi and Caffee 2013) with little solar wind addition prior to being ejected (Calzada-Diaz et al. 2016). Finally, the parent rock had a Moon–Earth transit time of a few million years before breaking up in the atmosphere into at least three pieces and landing in Antarctica ~0.7 Ma ago (Nishizumi and Caffee 2013). This likely did not induce high shock levels into the meteorites.

SUMMARY

Lunar meteorites MIL 090034, MIL 090070, and MIL 090075 are grouped specimens with similar compositions and textures. Feldspathic clast-rich impact melt breccia clasts are the dominant rock type found throughout the meteorites. These were likely derived from impact modification of precursor ferroan anorthosite lunar highland crustal rocks. The crust was modified in a large impact basin or cratering event, and subsequent modification occurred locally in the lunar highlands prior to ejection from the lunar surface.

The meteorites have been subject to varying levels of shock at the lunar surface, but average shock levels did not exceed ~25 GPa. FTIR spectroscopy, complemented by color CL-imaging, techniques can distinguish between anorthitic phases of different shock levels and estimate the peak shock pressures experienced by those phases. Furthermore, a ratio of the 1064/932 cm$^{-1}$ bands provides a good visual and quantifiable guide to the nature of feldspathic phases and hence, the range of peak shock pressures experienced by them. In addition to phase identification, mapping of thin sections using micro-FTIR proves to be a fast and reliable technique to scan samples in a nondestructive way to determine the degree of impact shock.

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**SUPPORTING INFORMATION**

Additional supporting information may be found in the online version of this article:

**Fig. S1** Labelled BSE image of MIL 090034.

**Fig. S2**. Labelled BSE image of MIL 090070.

**Fig. S3**. Labelled BSE image of MIL 090075.

**Fig. S4**. Fe/Mn ratio of cations in olivine crystal fragments in MIL 090034, 090070, and 090075.

**Fig. S5**. Fe/Mn ratio of cations in pyroxene crystal fragments in MIL 090034, 090070, and 090075.

**Table S1**. Electron microprobe composition data of the minerals and phases present in the samples of this study.

**Table S2**. FTIR spectral data of the map shown in Figure 6d. Each row corresponds to the spectrum of a single pixel whose location is indicated by in the final two columns.

**Table S3**. FTIR spectral data of the map shown in Figure 7d. Each row corresponds to the spectrum of a single pixel whose location is indicated by in the final two columns.

**Table S4**. FTIR spectral data of the map shown in Figure 8d. Each row corresponds to the spectrum of a single pixel whose location is indicated by in the final two columns.