

1 **Detecting Sub-Micron Space Weathering Effects in**  
2 **Lunar Grains with Synchrotron Infrared**  
3 **Nanospectroscopy**

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10 **Key Points:**

- 11 • Lunar soils were studied with spatially-resolved near-field spectroscopy in the mid-  
12 infrared  
13 • Spectral effects of space weathering were observed to vary continuously over a depth  
14 of 500 nm  
15 • Direct experimental evidence supports a connection between microstructural/chemical  
16 changes and mid-infrared effects in weathered lunar soil

## Abstract

Space weathering processes induce changes to the physical, chemical, and optical properties of space-exposed soil grains. For the Moon, space weathering causes reddening, darkening, and diminished contrast in reflectance spectra over visible and near-infrared wavelengths. The physical and chemical changes responsible for these optical effects occur on scales below the diffraction limit of traditional far-field spectroscopic techniques. Recently developed super-resolution spectroscopic techniques provide an opportunity to understand better the optical effects of space weathering on the sub-micrometer length scale. This paper uses synchrotron infrared nanospectroscopy to examine depth-profile samples from two mature lunar soils in the mid-infrared, 1500–700  $\text{cm}^{-1}$  (6.7–14.3  $\mu\text{m}$ ). Our findings are broadly consistent with prior bulk observations and theoretical models of space weathered spectra of lunar materials. These results provide a direct spatial link between the physical/chemical changes in space-exposed grain surfaces and spectral changes of space-weathered bodies.

## Plain Language Summary

The Moon’s surface, unprotected from the space environment, is bombarded with solar wind ions and micrometeoroids. These interactions are part of a process known as space weathering, which changes the physical and optical properties of lunar soils and asteroid surfaces on a microscopic scale. Technological hurdles have hindered our understanding of the connection between the physical changes caused by space weathering and the optical properties thought to result from them. Using synchrotron infrared nanospectroscopy, we examined how various weathering processes affect the infrared spectral characteristics of lunar soil grains. With these insights, we can develop better space weathering models to predict how different surfaces may be affected. The data from this investigation can also be used to calibrate laboratory analog studies of space weathering and help interpret observations of bodies similar to the Moon.

## 1 Introduction

The Moon is subject to frequent micrometeoroid impacts and bombardment by energetic solar wind ions. The compositional and structural changes induced by these processes on the Moon and other airless bodies are collectively referred to as space weathering (Hapke, 2001; Pieters et al., 1993). In aggregate, these changes to the morphology, chemical composition, and crystal structure of individual regolith grains alter the optical properties of the bulk soil — relative to freshly exposed lunar regolith, reflectance spectra of space exposed soils have reddened, darkened continua, and weaker diagnostic absorption peaks in the visible to infrared (IR) wavelengths. These effects have also been observed in studies of S-type asteroidal surface soils (Noguchi et al., 2011, 2014) and simulated space weathering experiments (Thompson et al., 2019; Kaluna et al., 2017; Lantz et al., 2017).

The effects of space weathering occur on a spatial scale comparable to the wavelength of visible light, presenting a unique challenge to our understanding of how various weathering processes evolve and interact to produce optical changes. The physical changes induced by space weathering, including the production of nano-phase iron particles and damage to the soil’s crystal structure (i.e., amorphization), have been found to occur predominantly within 100–200 nm of the grain surface (Pieters et al., 1993, 2000; Taylor et al., 2001; Noble et al., 2005). Hence, electron microscopy techniques are well-suited to characterize microstructural and micro-compositional changes. For instance, transmission electron microscopy (TEM) of weathered lunar soils has demonstrated that many of the optical changes seen in weathered soil are associated with the presence of nano-phase iron (npFe<sup>0</sup>) particles in amorphous rims coating mineral grains (Keller & McKay, 1993, 1997; Taylor et al., 2001, 2010), and micro-phase iron that occurs in ag-

67 glutinates (Basu, 2005). In particular,  $\text{npFe}^0$  grains smaller than 40 nm in diameter cause  
 68 spectral reddening and darkening, while larger iron particles cause only darkening (Noble  
 69 et al., 2007; Lucey & Riner, 2011). Although the physical and chemical changes caused  
 70 by space weathering can be detected via TEM, the localized optical effects of these changes  
 71 cannot be directly interrogated using diffraction-limited spectroscopic techniques. Tra-  
 72 ditional diffraction-limited spectroscopic techniques cannot spatially resolve features much  
 73 smaller than the wavelength of light used—most  $\text{npFe}^0$  is  $<40$  nm in diameter. Until re-  
 74 cently, computational modeling was required to determine the cumulative effects of space  
 75 weathering on the optical properties of lunar soil (Hapke, 2001; Lucey & Riner, 2011;  
 76 Lucey & Noble, 2008; Wohlfarth et al., 2019).

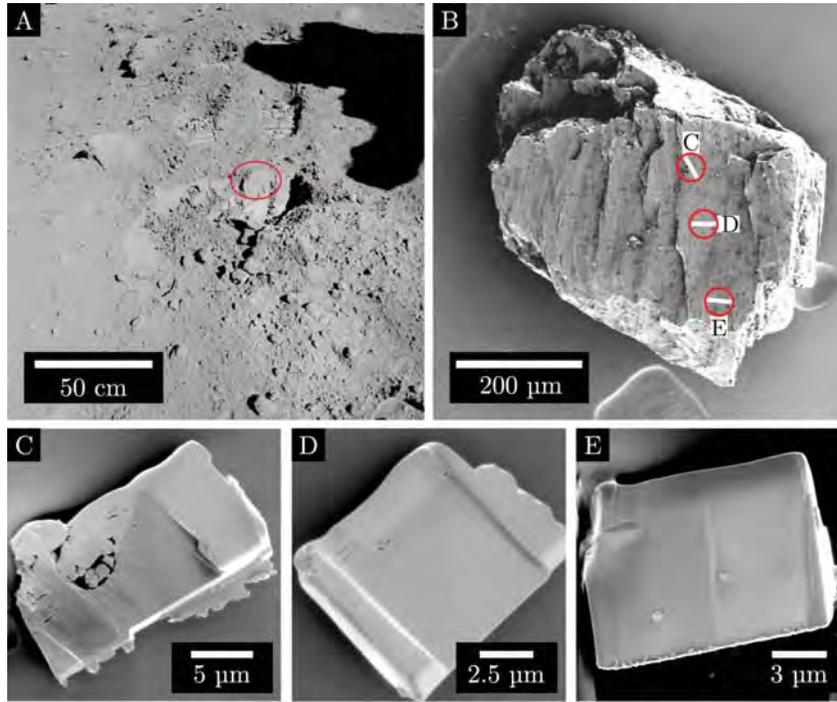
77 To bridge the gap between the optical effects of space weathering and the nano-  
 78 scale physio-chemical phenomena that produce them, we used Synchrotron Infrared Nano  
 79 Spectroscopy (SINS) to collect IR spectral data with sub-micrometer spatial resolution  
 80 from depth-profile samples of space-exposed lunar soil. This technique is capable of  $\sim 20$  nm  
 81 spatial resolution, making it possible to assess the optical effects of weathering phenom-  
 82 ena at a spatial resolution sufficient to resolve sub-micrometer products of lunar space  
 83 weathering (Bechtel et al., 2014). Near-field infrared spectroscopy has previously been  
 84 employed to analyze other extraterrestrial or planetary materials, including the Murchi-  
 85 son meteorite (CM2) (Kebukawa et al., 2010), a grain (Iris) from comet 81P/Wild 2 (Dominguez  
 86 et al., 2014), and the Didim meteorite (H3-5) (Yesiltas et al., 2020). This paper presents  
 87 near-field infrared spectroscopic evidence of space-weathering-induced changes to ma-  
 88 ture lunar soils’ optical properties in the ‘fingerprint region’ of the mid-infrared ( $1500\text{--}700\text{ cm}^{-1}$ ;  
 89  $6.7\text{--}14.3\ \mu\text{m}$ ).

## 90 2 Materials and Methods

### 91 2.1 Sample Preparation

92 The examined samples were selected from fine-grained portions of lunar soils 79221  
 93 and 10084, shown in Figures 1 and 2. The degree of surface exposure (maturity) of lun-  
 94 ar soils is typically indicated by the ferromagnetic resonance (FMR) surface exposure  
 95 index, given as FMR intensity divided by iron content ( $I_s/\text{FeO}$ )—see Morris (1976) for  
 96 more detail. By this metric, both 79221 and 10084 are highly mature soils with  $I_s/\text{FeO}$   
 97 values of 81 and 78, respectively (Rhodes & Blanchard, 1982; Taylor et al., 2001). To pre-  
 98 pare the soils for sectioning, we secured a portion of each sample to an aluminum stub  
 99 with carbon tape. We subsequently coated both sample and stub with  $\sim 10$  nm of gold-  
 100 palladium. The coated grains were imaged in secondary and back-scattered electrons us-  
 101 ing a Tescan Mira3 field-emission scanning electron microscope (FEG-SEM). An EDAX  
 102 energy-dispersive X-ray (EDX) spectrometer on the SEM was used for elemental anal-  
 103 yses and mineral identification.

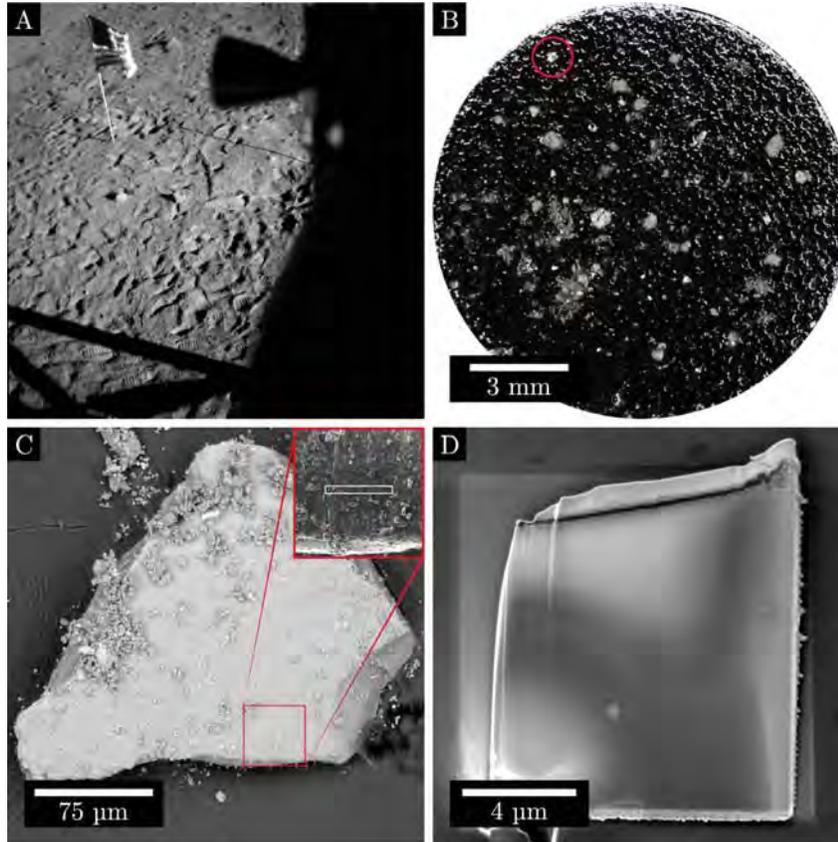
104 As described in greater detail below, SINS utilizes an atomic force microscope (AFM)  
 105 tip to enhance near-field resonances at a sample surface. To interrogate spectral response  
 106 changes as a function of depth, we created depth-profile lift-outs from the grains identi-  
 107 fied via SEM-EDX. Qualitative markers of space exposure (e.g., surface blistering, mi-  
 108 crometeoroid impact craters, melt splash) were used to inform the site-selection for tar-  
 109 geted liftout extraction. Lift-outs (initial thickness  $\approx 1\ \mu\text{m}$ ) were extracted from space-  
 110 exposed regions of the target grains with an FEI Quanta 3D focused ion beam (FIB) equipped  
 111 with a computer-controlled Omniprobe micro-manipulator. These samples were trans-  
 112 ferred to an Omniprobe lift-out grid, upon which they were thinned to a thickness of  $300\text{--}600$  nm.  
 113 Each sample was subsequently polished with a low-energy (5 kV, 48 pA)  $\text{Ga}^+$  beam for  
 114 roughly two minutes per side to remove any surface damage created during the thinning  
 115 procedure (Kato, 2004). The thinned lift-outs were then placed onto an ultra-flat (sur-  
 116 face roughness  $< 0.5$  nm) Si chip.



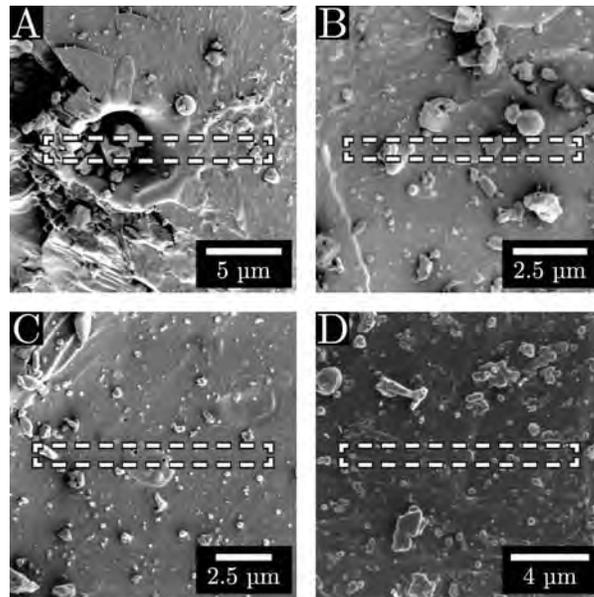
**Figure 1.** The geospatial context for lunar soil 79221 (Samples 1–3). (A) NASA photograph AS17-142-21827 showing approximate in situ sample location (circled) as recorded at the time of collection. (B) 2 kV SE image of host grain for samples 1–3, extracted from the circled areas. The encircled white rectangles indicate the orientation of each sample. (C)–(E) 2 kV SE images of samples 1–3, respectively, on Si substrate after thinning and low-voltage polishing.

**Table 1.** SEM-EDX compositions of the studied lunar samples.

Sample	Composition (atomic percent)						
	O	Mg	Al	Si	Ca	Ti	Fe
1–3	60%	—	16%	16%	8%	—	—
4	57%	6%	5%	17%	4%	3%	7%



**Figure 2.** (A) In situ sample location of lunar soil 10084 (sample 4) as recorded from the Apollo 11 lunar module. (B) Optical micrograph of grains from 10084 affixed to an SEM stub with carbon tape. Sample 4 was extracted from the circled grain. (C) Back-scattered electron (BSE) image (15 kV) of the target grain for sample 4 with higher-magnification secondary electron (SE) image inset. The white rectangle featured in the inset image denotes the FIB extraction site for sample 4. (D) 2 kV SE image of sample 4 on Si substrate after thinning and low- kV polishing by FIB.



**Figure 3.** Close-up SE images (2 kV) of the selected FIB extraction sites shown in Figure 1B and Figure 2C. A dashed rectangle indicates the location from which each sample was extracted. **(A)** Hypervelocity micrometeoroid impact crater sampled by sample 1 (79221). **(B)** The site selected for sample 2 (79221); displays evidence of surface blistering and includes two melt splash droplets. The left droplet contains vesiculated textures. **(C)** The extraction site for sample 3 (79221) includes a vesiculated melt-splash droplet. The surface of this region of the grain displays a lesser degree of blistering than at the extraction site for sample 2. **(D)** FIB extraction site for sample 4 (10084), selected to include small melt splash droplets and mild surface blistering and amorphization.

117 Samples 1–3 were taken from a  $\sim 250\ \mu\text{m}$  grain of 79221 with a composition con-  
 118 sistent with anorthite-rich plagioclase (see Table 1). Sample 4 was extracted from a  $\sim 150\ \mu\text{m}$   
 119 grain of 10084 with a composition consistent with Ti-, Al-rich augite, in agreement with  
 120 prior studies of this sample and other Apollo 11 lunar rock samples (Ross et al., 1970).  
 121 A fifth sample was taken from a terrestrial anorthite standard (Miyake Island, Japan).  
 122 The studied samples and their characteristics are outlined in Table 2.

**Table 2.** Descriptions of studied samples

Sample	Soil	Composition	Description
1	79221	An-rich Plagioclase	Micrometeoroid impact crater
2	79221	An-rich Plagioclase	Melt-splash coated
3	79221	An-rich Plagioclase	Surface blistering
4	10084	Ti-, Al-rich Augite	Mildly amorphized surface
—	—	Anorthite	Terrestrial mineral standard

## 123 2.2 Experimental Methods

124 Near-field IR spectra were collected using SINS at Beamline 5.4 at the Advanced  
 125 Light Source (Bechtel et al., 2014). This technique can be thought of as a combination  
 126 of Fourier-transform infrared spectroscopy (FTIR), scattering-type scanning optical mi-  
 127 croscopic (s-SNOM) techniques, and atomic force microscopy (AFM). Synchrotron IR  
 128 light is coupled into an asymmetric Michelson interferometer consisting of a beamsplit-  
 129 ter (KBr), a moving mirror (Nicolet 6700 FTIR spectrometer), and an AFM (Bruker In-  
 130 nova). Light is focused onto an oscillating AFM tip in one arm of the interferometer. The  
 131 light scattered by the tip is combined with light reflecting off the moving mirror in the  
 132 interferometer’s second arm. The resulting interference signal is detected on a mercury  
 133 cadmium telluride (HgCdTe) detector. With this experimental setup, the spatial reso-  
 134 lution is determined by the radius of curvature of the AFM tip used (25 nm in this case)  
 135 and is independent of the wavelength of the incident light.

136 The data presented in this work were collected over a broad range of mid-infrared  
 137 wavenumbers,  $5000\text{--}700\ \text{cm}^{-1}$  ( $2.0\text{--}14.3\ \mu\text{m}$ ), with a spectral resolution of  $8\ \text{cm}^{-1}$ . At shorter  
 138 wavelengths, however, the signal is dominated by noise caused by reduced tip-sample cou-  
 139 pling. This high-frequency noise precludes the identification of any C-H or O-H stretch  
 140 features in the sample spectra. As such, this work focuses primarily on the “fingerprint”  
 141 region,  $1500\text{--}700\ \text{cm}^{-1}$  ( $6.7\text{--}14.3\ \mu\text{m}$ ). This range captures key features in the infrared  
 142 spectra of both plagioclase and pyroxene while maximizing the signal-to-noise ratio. Of  
 143 particular interest to lunar and remote-sensing applications, the explored spectral range  
 144 encompasses the Christiansen feature — an important diagnostic feature in mid-infrared  
 145 silicate spectra. Canonically, the CF is defined as an emissivity maximum associated with  
 146 the frequency at which the real part of the effective dielectric constant (index of refraction)  
 147 approaches unity (Christiansen, 1884). Since this condition occurs at wavelengths  
 148 just short of the fundamental modes, the CF contains valuable information about sil-  
 149 icate mineral composition (Salisbury et al., 1997; Conel, 1969).

150 To differentiate the near-field signal from the far-field (scattered) background, sig-  
 151 nals are detected at higher harmonics of the tip oscillation frequency, which arise from  
 152 the non-linear near-field response. Here, we use the second harmonic response as a com-  
 153 promise between background suppression and signal-to-noise ratio. After demodulation,  
 154 the interferometric signal is Fourier transformed to yield the complex near-field spectra.  
 155 To first-order approximation, the spectral amplitude,  $|A(\tilde{\nu})|$ , is related to the real-valued  
 156 component of the material’s complex dielectric function (i.e., the reflection coefficient)

157 and the spectral phase,  $\Phi(\tilde{\nu})$ , is similarly related to the imaginary component of the di-  
 158 electric function (i.e., the absorption coefficient) (Xu et al., 2012; Govyadinov et al., 2014).  
 159 However, this approximation may not be strictly valid due to the thickness of the sam-  
 160 ples studied, the presence of nanoscale heterogeneities therein, and variable oscillator strengths.  
 161 Spectral features may therefore be shifted compared to conventional FTIR measurements  
 162 (Mastel et al., 2015).

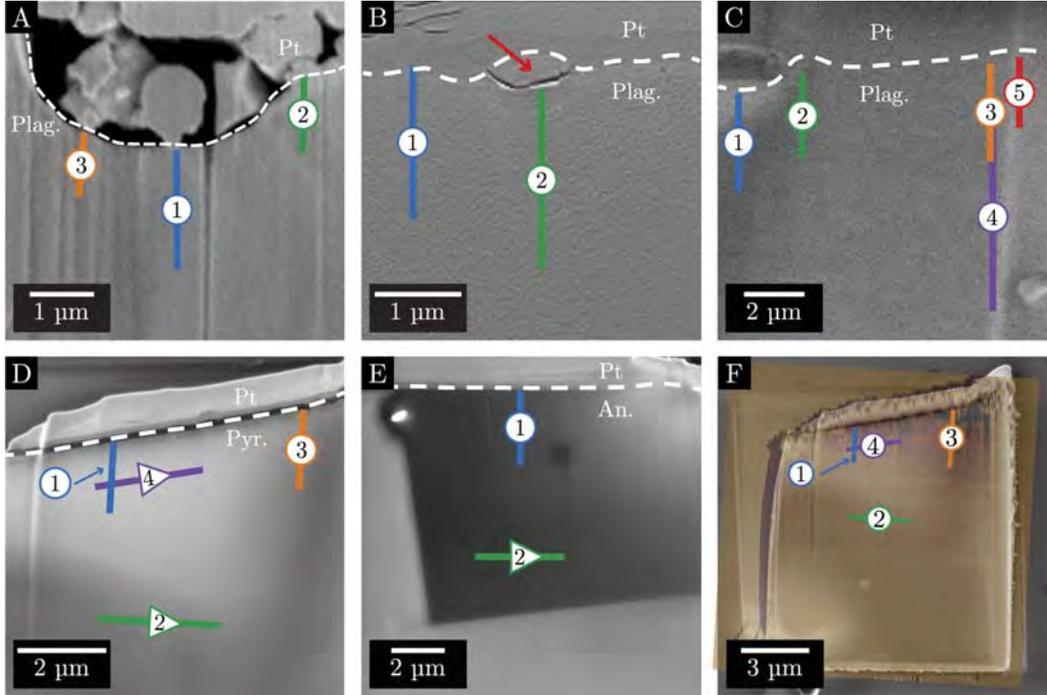
163 We collected a series of line scans oriented perpendicular to the space-exposed sur-  
 164 face (vertically) to interrogate the effects of space weathering as a function of depth. Each  
 165 line scan is composed of 20–60 evenly-distributed points with an inter-point spacing of  
 166 20–100 nm. Three horizontally-oriented (i.e., parallel to the grain surface) scans were col-  
 167 lected to rule out systematic instrumental artifacts as the cause of observed depth-dependent  
 168 changes. Background spectra were collected before and after each line scan. The exper-  
 169 imental spectra were referenced to the average over relevant backgrounds. The location  
 170 and orientation of each line scan are shown in Figure 4 and further details can be found  
 171 in Table 3.

**Table 3.** Parameters for each line scan performed. Italic text denotes horizontally-oriented scans (i.e., parallel to the space-exposed surface). Spectra were collected with  $8\text{ cm}^{-1}$  spectral resolution. At each point, a 500-scan measurement was collected over roughly six minutes. Backgrounds were collected before and after each line scan.

Sample	Scan	Length ( $\mu\text{m}$ )	Points	Spacing (nm)	Depth(s)
1	1	1.70	18	95	0 – 1.70 $\mu\text{m}$
	2	1.18	22	55	0 – 1.18 $\mu\text{m}$
	3	0.89	14	65	0 – 0.89 $\mu\text{m}$
2	1	1.93	22	90	0 – 1.93 $\mu\text{m}$
	2	1.61	21	75	0 – 1.61 $\mu\text{m}$
3	1	0.52	5	105	0 – 0.52 $\mu\text{m}$
	2	1.28	18	70	0.10 – 1.38 $\mu\text{m}$
	3	1.28	65	20	0.34 – 1.62 $\mu\text{m}$
	4	2.45	50	50	2.34 – 4.79 $\mu\text{m}$
	5	0.75	11	70	30 – 750 nm
4	1	0.77	17	45	0 – 770 nm
	2	1.45	29	50	4.08 – 4.64 $\mu\text{m}$
	3	0.80	17	45	0 – 800 nm
	4	0.89	30	30	1.02 $\mu\text{m}$
Anorthite	1	1.84	24	75	0 – 1.84 $\mu\text{m}$
Standard	2	1.90	20	95	6.35 $\mu\text{m}$

### 172 2.3 Data Analysis

The data presented in this work were pre-processed using a custom program that employs commercially available fast Fourier transform software packages (Wavemetrics Igor Pro). Background and instrumental responses were removed by referencing the amplitude and phase signals to a background spectrum collected on Si or Au before and after each sample scan. The referenced amplitude and phase signals were obtained via, re-



**Figure 4.** Close-up SE images (2kV) of the samples shown in Figure 1C–F and Figure 2D, upon which each line scan site is superimposed. The direction of the scans oriented parallel to the space-exposed surface is indicated with an arrow. All vertically-oriented scans start in the grain interior and end near the surface. **(A)** Sample 1 (79221), scans 1–3. **(B)** Sample 2 (79221), scans 1 and 2. The second scan on this sample is located below a melt-droplet (indicated by the red arrow) that was adhered to the surface. **(C)** Sample 3 (79221), scans 1–5. The first and second scans are located below an unusually thick vesiculated melt texture. Note that scan 4 ends roughly  $2.4\ \mu\text{m}$  from the surface. **(D)** Sample 4 (10084), scans 1–4. The first and third scans are oriented vertically, whereas scans 2 and 4 were collected parallel to the grain surface at different depths. **(E)** Scans 1 and 2 from the terrestrial anorthite standard, respectively oriented vertically and horizontally. Note that the discoloration (the dark square in the upper right) is a temporary charging effect caused by  $\text{Ga}^+$  ion beam use immediately prior to image capture. **(F)** An example demonstrating the alignment of the AFM topographical image (overlaid at 50% opacity) over a reference 2kV SE image. We found general agreement in all AFM channels (i.e., tapping phase, amplitude, and topography), regarding the position of each scan and the Pt cap. However, the topographical image was used for navigation and is thus shown here.

spectively,

$$|A(\tilde{\nu})| = \frac{|A(\tilde{\nu})|_{\text{sample}}}{|A(\tilde{\nu})|_{\text{reference}}} \quad \text{and} \quad \Phi(\tilde{\nu}) = \Phi(\tilde{\nu})_{\text{sample}} - \Phi(\tilde{\nu})_{\text{reference}}. \quad (1)$$

173 SINS amplitude spectra are generally more susceptible to topographical and instru-  
 174 mental artifacts than phase spectra. This susceptibility is partly because amplitude spec-  
 175 tra typically present dispersive lineshapes, whereas phase spectra generally occur as Gaus-  
 176 sian or Lorentzian profiles, potentially making weak features more difficult to see in am-  
 177 plitude data. Phase spectra have been shown to closely track the material’s local absorp-  
 178 tion coefficient (Stiegler et al., 2011; Taubner et al., 2004), which is crucial for the depth-  
 179 profile studies in this work. As such, we will focus primarily on phase spectra to exam-  
 180 ine the relative changes of particular spectral features as a function of depth.

181 The collection depth for each spectrum was calculated relative to the bottom edge  
 182 of the protective Pt cap. The interface of the space-exposed surface and the Pt cap was  
 183 located by overlaying high-resolution SE images (in which the Pt was visually distinct  
 184 from the sample) atop the AFM topographical images used for SINS target selection.  
 185 Spectra collected from the Pt cap were not used for the analyses described below. Fig-  
 186 ure 4F is an example of the alignment of topographical and SE images.

187 To assess the validity of the observed qualitative spectral changes over depth, we  
 188 used a robust, iterative, non-linear least-squares fitting (or peak deconvolution) algorithm.  
 189 Peaks in phase spectra were fit to Lorentzians with a linear baseline, following the Lorentz  
 190 model for dielectrics. The constraints and initial values used for the fitting procedure were  
 191 similarly physically motivated. Together, these factors improved the efficiency and like-  
 192 lihood of convergence for our analyses. This approach is loosely similar to the Modified  
 193 Gaussian Model (MGM) developed by Sunshine, Pieters, & Pratt, 1990, with some fun-  
 194 damental changes implemented to account for the differences between SINS and far-field  
 195 infrared spectroscopy. It should be noted that the MGM, however, is typically used with  
 196 UV-visible or near infrared data. Similar fitting procedures have been used previously  
 197 to analyze a suite of extraterrestrial materials such as Martian meteorites (Sunshine et  
 198 al., 1993), remote sensing data from Mars (Mustard & Sunshine, 1995), and lunar soils  
 199 (including the two soils studied here) (Noble et al., 2006). For a more thorough treat-  
 200 ment of our quantitative model, please refer to the Supplementary Material.

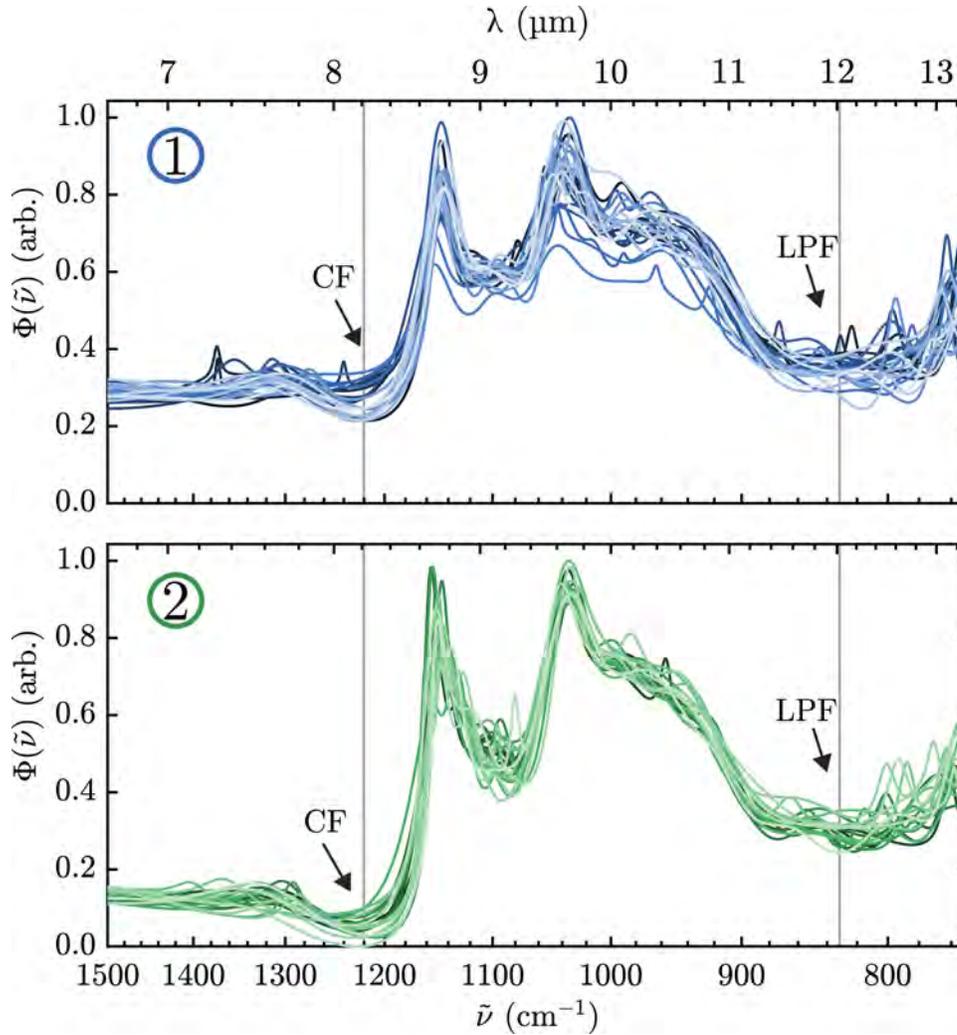
## 201 2.4 Terrestrial Standard

202 For purposes of comparison, two scans were collected from a terrestrial anorthite  
 203 standard. The phase spectra from these two scans are plotted in Figure 5. Spectra from  
 204 the anorthite standard feature two strong absorption peaks likely corresponding to Si-  
 205 O-Si asymmetric stretch Reststrahlen bands (Le Bras et al., 2003; Carmichael, 1988). The  
 206 peak at approximately  $1150 \text{ cm}^{-1}$  ( $8.70 \mu\text{m}$ ) is sharp and distinct ( $\text{FWHM} \approx 60 \text{ cm}^{-1}$ ),  
 207 whereas the peak at roughly  $1035 \text{ cm}^{-1}$  ( $9.66 \mu\text{m}$ ) is substantially broader ( $\text{FWHM} \approx$   
 208  $170 \text{ cm}^{-1}$ ) due to the presence of a shoulder roughly centered about  $965 \text{ cm}^{-1}$  ( $10.36 \mu\text{m}$ ).  
 209 These features’ positions and lineshapes closely match previously reported absorption  
 210 spectra for anorthite-rich plagioclase (Estep et al., 1971; Williams & Jeanloz, 1989). Given  
 211 this correspondence, the shallow trough at approximately  $1230 \text{ cm}^{-1}$  is likely related to  
 212 the CF. Accordingly, the broad minimum centered at  $\sim 840 \text{ cm}^{-1}$  is likely associated with  
 213 a low-phase feature between vibrational modes.

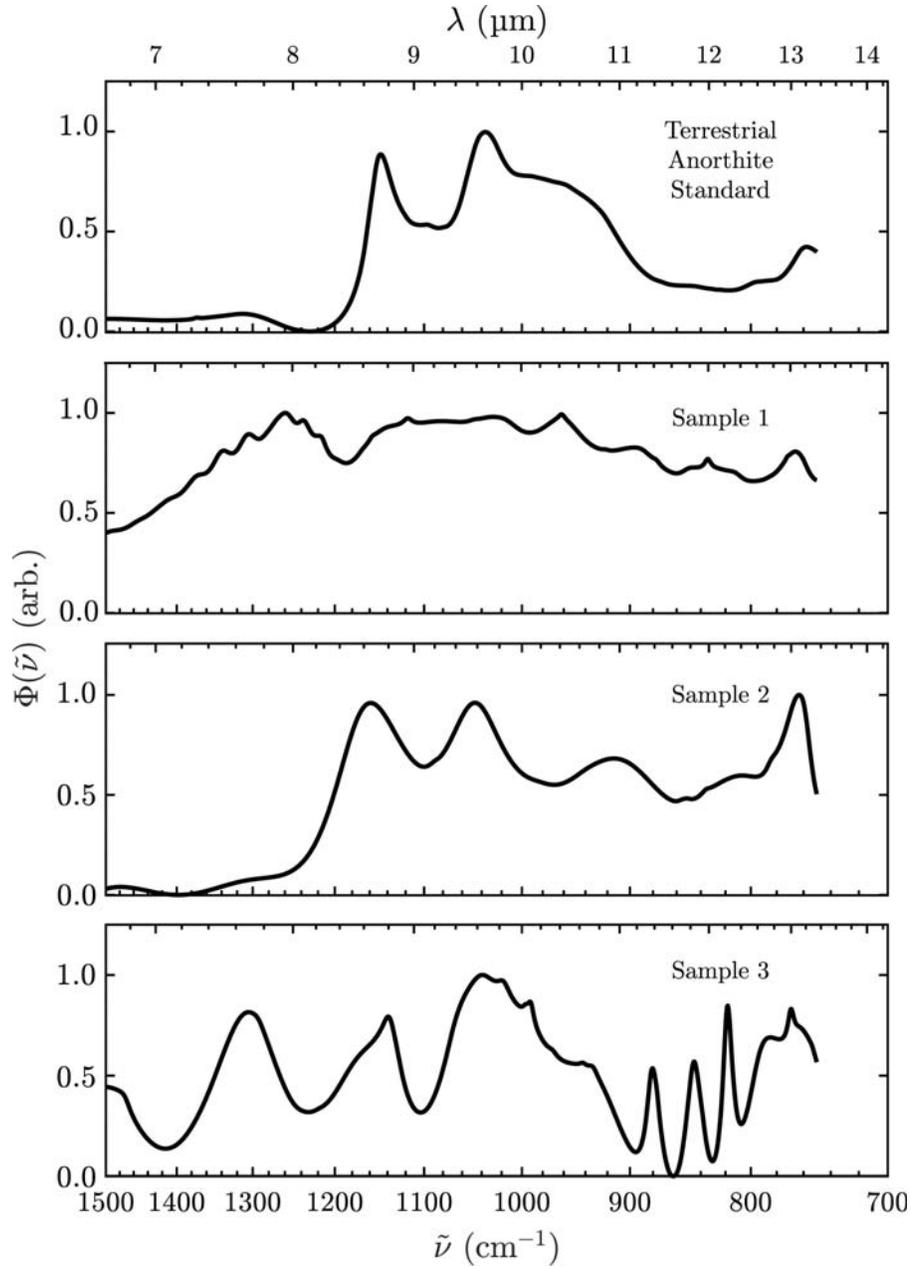
214 The SINS phase spectra from samples 1–3 are qualitatively similar to those from  
 215 the (identically-prepared) terrestrial anorthite standard. The similarity of these spectra  
 216 varies from sample to sample, as shown in Fig. 6. Spectra from samples 2 and 3 include  
 217 the two major features seen in the standard (peaks at roughly  $1040 \text{ cm}^{-1}$  and  $1150 \text{ cm}^{-1}$ ),  
 218 but also contain some features not observed for the terrestrial standard. By contrast, sam-  
 219 ple 1 is characterized by spectra with relatively weak and broad features, making detailed

220 interpretation challenging. Potential explanations for this divergence are explored fur-  
 221 ther in the Discussion.

222 The depth-dependent spectral effects seen among samples from 79221 were not ob-  
 223 served in spectra collected from the mineral standard, indicating that they are unlikely  
 224 to have arisen due to instrumental effects (see Fig. 5). Moreover, line scans collected from  
 225 the terrestrial standard at a constant depth were not found to differ significantly from  
 226 those collected at variable depths, offering supporting evidence that the observed vari-  
 227 ations result from space weathering-induced microstructural and chemical changes in the  
 uppermost layers of lunar soil grains.



**Figure 5.** Line scan phase spectra collected on the terrestrial anorthite standard. Scan 1 (top panel, plotted in blue) is oriented perpendicular to the surface and starts in the grain interior. Scan 2 (bottom panel, plotted in green) is oriented parallel to the grain surface. Spectra collected at depth are plotted in darker colors, whereas the lighter colors indicate spectra collected from near the surface. The Christiansen feature (CF) and a low-phase feature (LPF) are indicated with arrows.



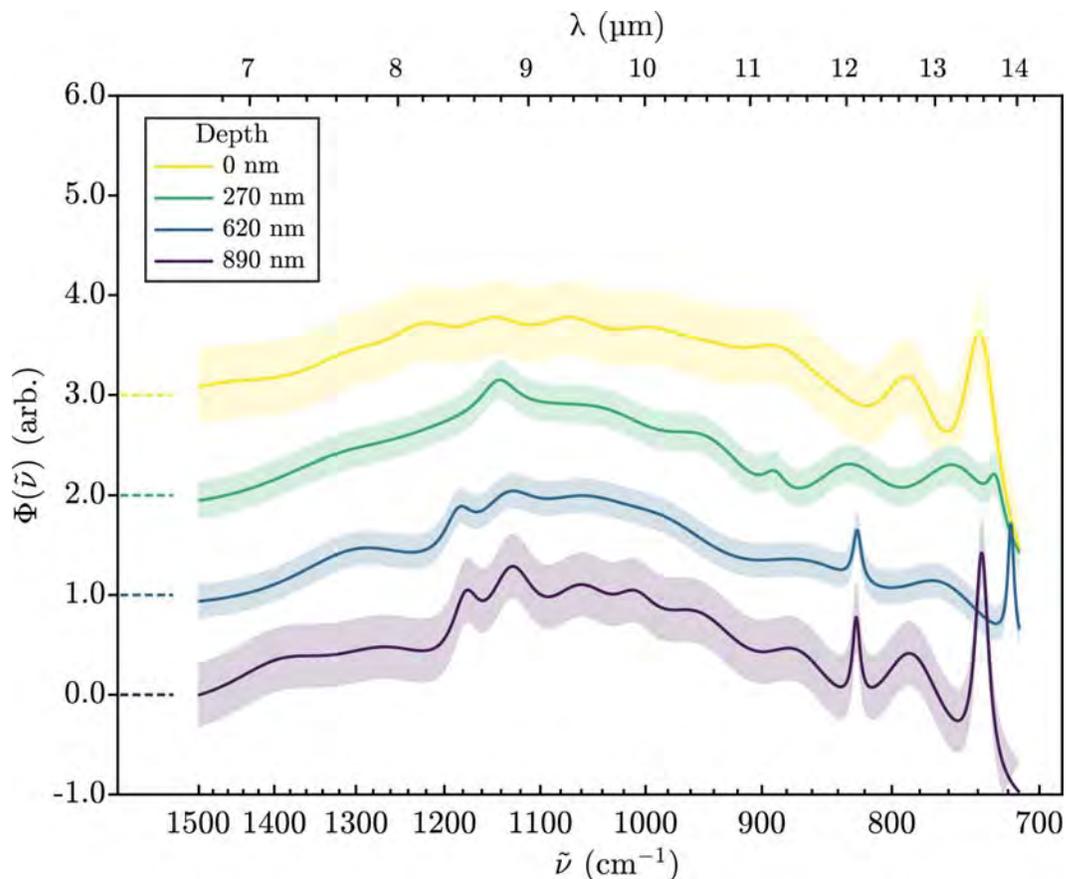
**Figure 6.** Comparing the average SINS phase spectra of the interiors of samples 1–3 (79221) to the terrestrial anorthite standard (Miyake, Japan). The spectra plotted for samples 1–3 are averages over the deepest portions of each line scan. The phase spectrum for the terrestrial anorthite standard is the average of all spectra from that sample.

### 3 Results

#### 3.1 Micrometeoroid Impact Crater (Sample 1)

SINS phase spectra,  $\Phi(\tilde{\nu})$ , collected near the hypervelocity impact crater on sample 1 (see Fig. 3) exhibit systematic variations between the grain interior (far from the crater bottom) and the grain surface (just below the crater). Primary among these variations is the loss of spectral contrast with increasing proximity to the surface, as shown in Figure 7 and described below.

Two peaks in the phase spectra at  $830\text{ cm}^{-1}$  ( $12.05\text{ }\mu\text{m}$ ) and  $1140\text{ cm}^{-1}$  ( $8.77\text{ }\mu\text{m}$ ) broaden and display reduced spectral contrast with increasing proximity to the surface. These effects are most notable within  $300\text{ nm}$  of the surface for both features. Near the surface, the loss of spectral contrast causes the CF to become indistinguishable from the background.



**Figure 7.** Computed fits of selected SINS phase spectra from scan 3 on sample 1, collected at the labeled distances from the bottom of the hypervelocity impact crater on the plagioclase grain shown in Fig. 3A and Fig. 4A. Spectra are vertically offset (dashed lines) from one another for clarity. Shaded areas indicate  $2\sigma$  confidence intervals. Diminished spectral contrast was observed among spectra from close to the surface, particularly for key spectral features at  $830\text{ cm}^{-1}$  ( $12.05\text{ }\mu\text{m}$ ) and  $1140\text{ cm}^{-1}$  ( $8.77\text{ }\mu\text{m}$ ).

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### 3.2 Melt-Splash Coating (Sample 2)

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Sample 2 was collected from a melt-splash coated region approximately  $150\ \mu\text{m}$  from the hypervelocity impact crater on sample 1 (see Fig. 3). The spectra from this sample are less noisy and contain sharper peaks than those described in Subsection 3.1. As shown in Figure 8, these spectra evolve as a function of depth similar to those from sample 1. We observed depth-dependent loss of spectral contrast, particularly at longer wavelengths. This effect is most prominent among spectra collected from within  $400\ \text{nm}$  of the surface.

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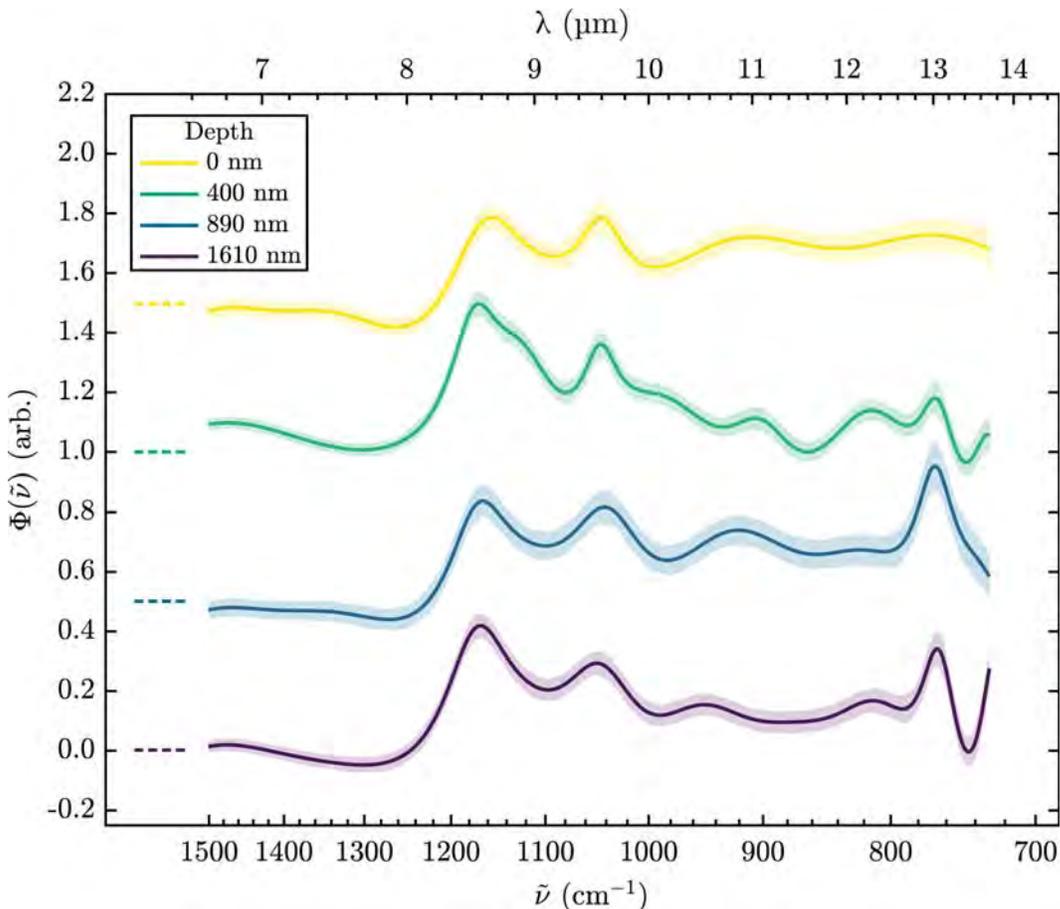
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Spectra from the grain interior include several peaks in the range  $\sim 950\text{--}725\ \text{cm}^{-1}$ . At the surface, these features are difficult to distinguish from the background conclusively. The provenance of these features is explored further in the discussion. A ‘reddening’ baseline accompanies this trend at wavelengths  $\gtrsim 11\ \mu\text{m}$ , wherein the apparent slope transitions from negative to slightly positive between depths of  $890\ \text{nm}$  and  $400\ \text{nm}$ . Two prominent peaks occur at  $1045\ \text{cm}^{-1}$  ( $9.6\ \mu\text{m}$ ) and  $1165\ \text{cm}^{-1}$  ( $8.6\ \mu\text{m}$ ) in spectra from all sampled depths. These features remain relatively stable over depth, with only some statistically insignificant broadening observed near the surface.



**Figure 8.** Computed fits of selected SINS phase spectra from scan 2 on sample 2, collected at the labeled distances from the melt-splashed surface of the plagioclase grain shown in Fig. 3B and Fig. 4B. Spectra are vertically offset (dashed lines) from one another for clarity. Shaded areas indicate  $2\sigma$  confidence intervals. Diminished spectral contrast was observed close to the surface for some features. Key spectral features at  $1045\ \text{cm}^{-1}$  and  $1165\ \text{cm}^{-1}$  are discussed in greater detail in the text.

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### 3.3 Surface Blistering (Sample 3)

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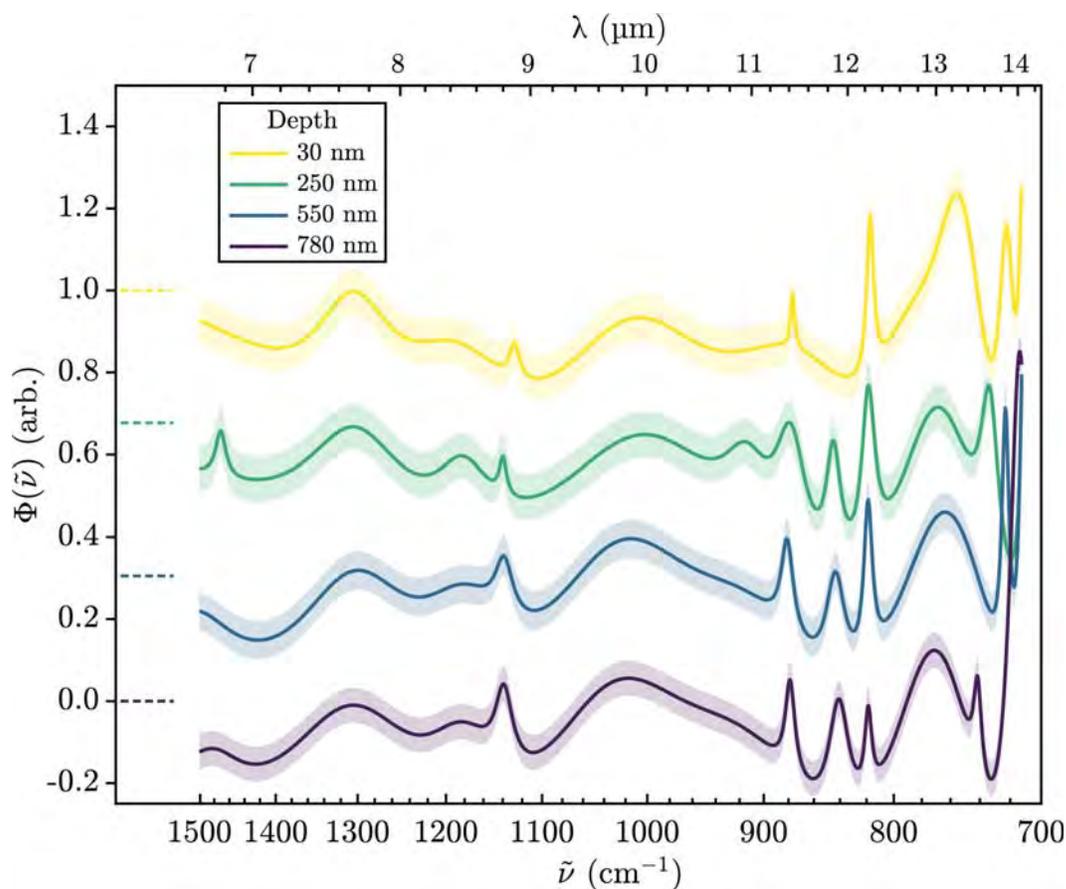
The spectra from sample 3, characterized by its evidence of surface blistering (see Fig. 3), are shown in Figure 9. We observed depth-dependent loss of spectral contrast, particularly at wavelengths of 8.5–12  $\mu\text{m}$ . This effect is most prominent among spectra collected from within 250 nm of the surface.

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Importantly, this sample's spectra contain features consistent with imperfect background subtraction. In particular, the peak at  $\sim 1350\text{ cm}^{-1}$  is consistent with some signal from the silicon substrate 'bleeding through' the sample. In contrast to the sample's diagnostic features, this peak is stronger at the surface than in the grain interior.



**Figure 9.** Computed fits of selected SINS phase spectra from scan 5 on sample 3, collected at the labeled distances from the blistered surface of the plagioclase grain shown in Fig. 3C and Fig. 4C. Spectra are vertically offset (dashed lines) from one another for clarity. Shaded areas indicate  $2\sigma$  confidence intervals. Diminished spectral contrast was observed at the surface for several diagnostic features. Key spectral features at  $750\text{ cm}^{-1}$ ,  $1015\text{ cm}^{-1}$  and  $1145\text{ cm}^{-1}$  are discussed in greater detail in the text.

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### 3.4 Mildly Amorphized Pyroxene (Sample 4)

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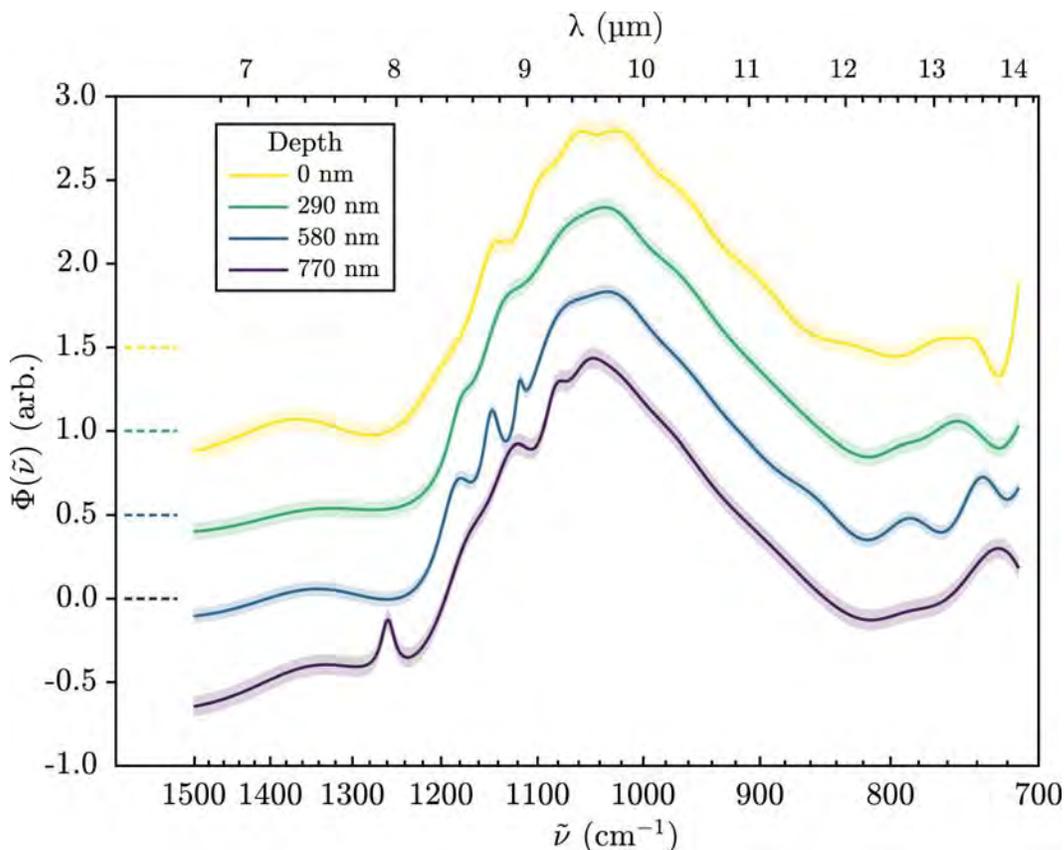
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**Figure 10.** Computed fits of selected SINS phase spectra from scan 1 on sample 4 at a range of depths from the blistered surface (see Fig. 3D). Spectra are vertically offset (dashed lines) from one another for clarity. Shaded areas indicate  $2\sigma$  confidence intervals. Spectral features were not observed to undergo substantial changes over depth, as discussed in greater detail within the text.

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### 3.5 Depth-Dependent Spectral Effects

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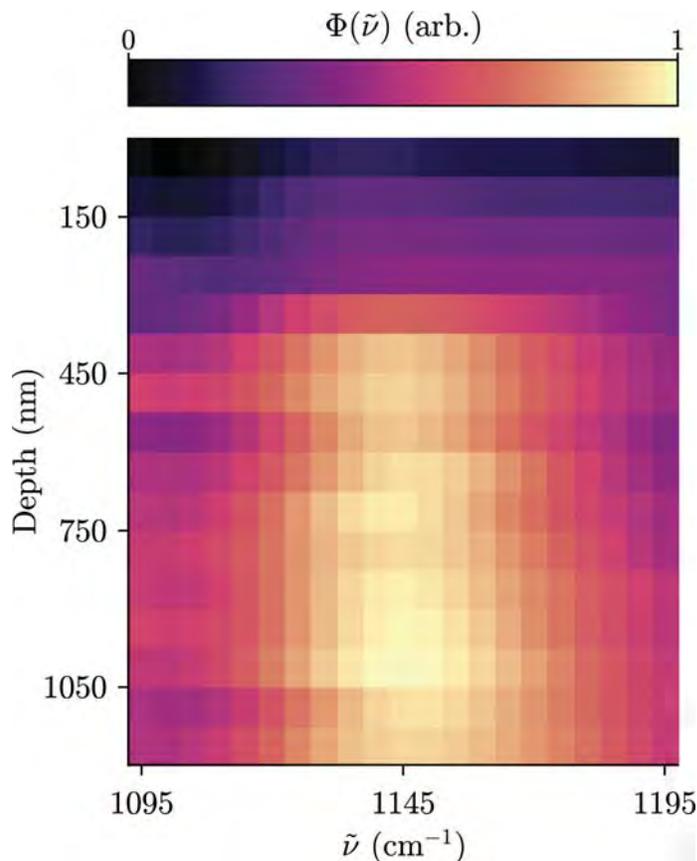
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The collected data for samples 2 and 3 indicate that the total scattered intensity and spectral contrast are inversely correlated with distance from the space-exposed surface. Peaks present in SINS amplitude spectra from close to the surface of these two samples are significantly less distinguishable from the continuum than in spectra collected

281 from the crystalline grain interior (see, e.g., Fig. 8). Figure 11 illustrates this effect cen-  
 282 tered about a peak at  $1145\text{ cm}^{-1}$  found in the phase spectra of sample 3. In scans from  
 283 sample 2, peaks at higher wavenumbers were more effectively suppressed than those at  
 lower wavenumbers. Whether this trend extends to samples 1 and 4 remains unclear.



**Figure 11.** Color-map demonstrating the observed relationship between spectral contrast and surface proximity for the peak at roughly  $1150\text{ cm}^{-1}$  in SINS phase spectra from sample 3 (see Fig. 9 and Fig. 4E). The data for each of the five scans shown in Fig. 4C were binned by depth (16 bins, 75 nm per bin) and wavenumber (20 bins,  $5\text{ cm}^{-1}$  per bin). The pixel color corresponds to the average value of the continuum-removed  $\Phi(\tilde{\nu})$  spectra from the five line scans on sample 3, for the corresponding wavenumbers and depths. The effect size is markedly greater within the uppermost 300 nm of the sample, consistent with surface-correlated weathering phenomena

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285 The integrated amplitude response, analogous to total scattered intensity, was obser-  
 286 ved to evolve over depth (see Figure 12). This quantity was calculated for each col-  
 287 lected spectrum by integrating the amplitude signal over the wavenumbers of interest  
 288 ( $\nu \in [700\text{ cm}^{-1} 2000\text{ cm}^{-1}]$ ). In scans from samples 1–3, the total scattered intensity  
 289 is strongly correlated with depth (i.e., spectra from close to the space-exposed surface  
 290 are darker than those from within the grain interior). This darkening effect occurs in sam-  
 291 ples 1–3 over depths of 0–2000 nm. In samples 2 and 3, darkening is most pronounced  
 292 in the uppermost 500 nm. Interestingly, the darkening in spectra from near the impact  
 293 crater (sample 1) occurs at a shallower slope than the other 79221 samples.

294 Data from sample 4 do not display a strong correlation between scattered inten-  
 295 sity and depth.

## 296 4 Discussion

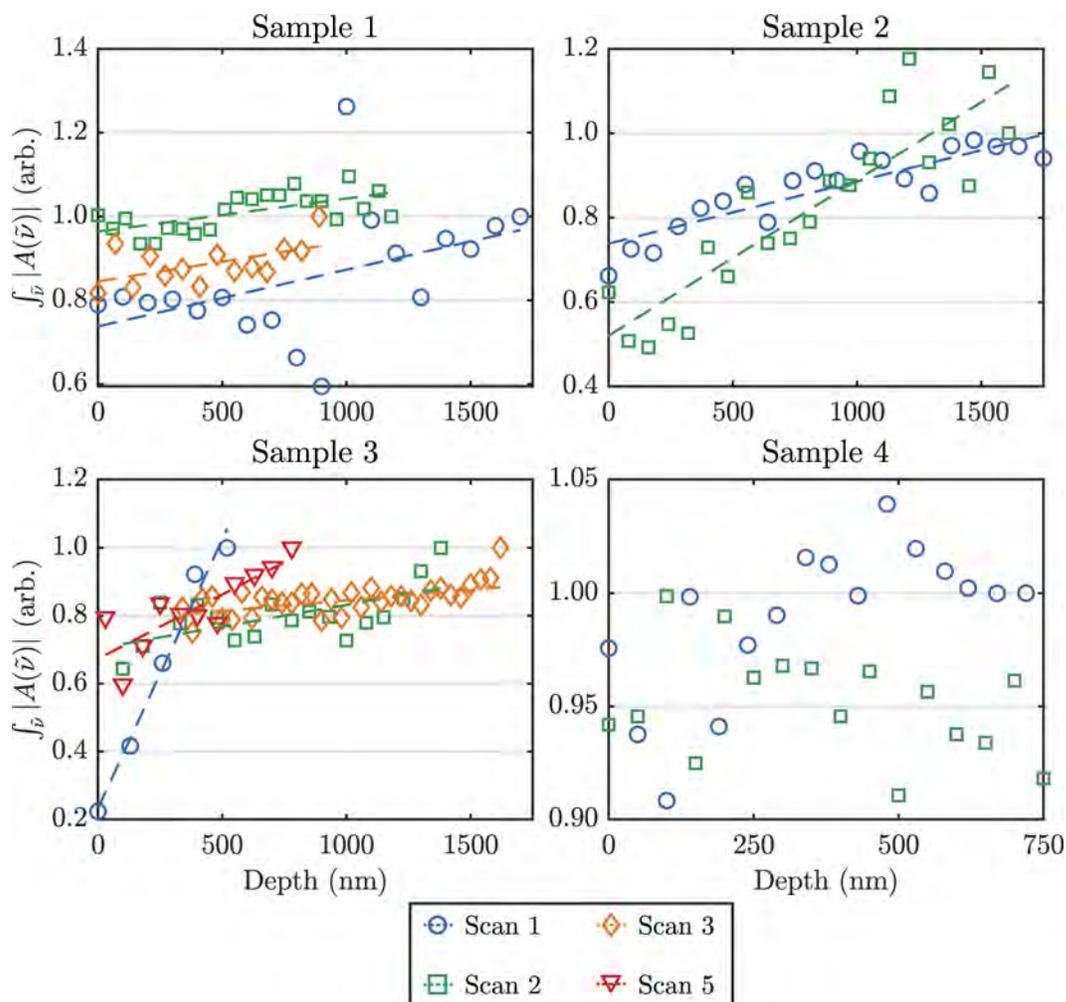
297 Many minerals have qualitatively different near-field and far-field IR spectra. Though  
 298 the two spectra may share some features, there is generally no one-to-one correlation (Hermann  
 299 et al., 2014; Huth et al., 2012; Pollard et al., 2015). This disparity means that we can-  
 300 not definitively link spectral features observed in our samples to particular vibrational  
 301 modes without further analysis. Despite this, many of the features we observed in our  
 302 samples' SINS spectra are consistent with the characteristic absorption features reported  
 303 in the literature.

304 The  $\sim 830\text{ cm}^{-1}$  feature observed with varying prominence in samples 1–3 appear  
 305 to be related to the Si-O-Si or Al-O symmetric stretch features. Although prior work mod-  
 306 eling the optical constants of labradorite has not found a similar peak at roughly  $830\text{ cm}^{-1}$   
 307 ( $12.05\text{ }\mu\text{m}$ ) in spectra of the complex coefficient (Ye et al., 2019), these peaks are present  
 308 in a majority of the spectra from samples 1–3 and appear to follow a depth-dependent  
 309 trend similar to other peaks. Similar features have additionally been reported in mid-  
 310 infrared absorption spectra of anorthite and albite (Dorschner, 1971). That this feature  
 311 is more pronounced for these samples result from the presence of the hypervelocity im-  
 312 pact crater on the host grain for samples 1–3 and the high Al-content relative to other  
 313 plagioclase minerals. Al-O<sub>4</sub> tetrahedra are more susceptible to deformation under pres-  
 314 sure than their Si-O<sub>4</sub> counterparts (Johnson et al., 2003; Williams & Jeanloz, 1989; Williams,  
 315 1998). It has been speculated that (Si, Al)-O<sub>4</sub> tetrahedra are susceptible to metastable  
 316 ‘defects’ under pressure that lead to, for example, Si-O-Si links between adjacent tetra-  
 317 hedra that may alter the stretch and bending vibrational modes (Santamaria-Perez et  
 318 al., 2016). Alternatively, it is hypothetically possible that these peaks could be an indi-  
 319 cation of silanol (Si-O-H) that formed on the surface of the sample or on the sub-  
 320 strate underneath the sample. Since the spectra were normalized to an average of stan-  
 321 dard spectra, which included scans collected on the Si-chip or nearby platinum cap, this  
 322 scenario is highly unlikely.

323 Both soils 79221 and 10084 are classified as mature, with FMR maturity indices  
 324 of  $I_s/\text{FeO} = 81$  and  $75$ , respectively (Morris, 1978). However, the maturity index is by  
 325 definition a bulk property of soils. As such, the individual grains that comprise a mat-  
 326 ure soil are likely to have various exposure ages. Although sample 4 displays far less pro-  
 327 nounced space weathering effects than samples 1–3, this is more likely to be a reflection  
 328 of the different mineral chemistry.

329 Previous studies on experimentally shocked feldspars have shown that absorption  
 330 bands weaken and broaden due to increasing glass content, particularly at shock pres-  
 331 sures above  $\sim 20\text{ GPa}$  (Nash et al., 1993; Johnson et al., 2002, 2003). In contrast, pyrox-  
 332 enes are more resilient to increasing shock pressures. Studies show little change in spec-  
 333 tral properties with shock pressures of  $45\text{ GPa}$  and up to  $65\text{ GPa}$  (Adams et al., 1979;  
 334 Johnson et al., 2002).

335 Shock effects may also be responsible for the apparent dissimilarity between spec-  
 336 tra from sample 1 and those from the anorthite standard. The region directly below the  
 337 micrometeoroid impact crater (on sample 1) experienced much greater pressures than  
 338 the material in samples 2 and 3. The most prominent feature at roughly  $1100\text{ cm}^{-1}$  in  
 339 phase spectra from sample 1 may result from a shock-induced spectral broadening of the  
 340  $1000\text{ cm}^{-1}$  and  $1150\text{ cm}^{-1}$  features seen for samples 2–3 and the terrestrial anorthite stan-  
 341 dard. These differences could alternatively be explained by the presence of compositional  
 342 or structural inhomogeneities in the soil grain. Should this interpretation be correct, our  
 343 observations serve to reinforce the value of SINS for spectroscopic investigation of micrometer-



**Figure 12.** The amplitude response for each collected spectrum, integrated over the range  $\nu \in [700 \text{ cm}^{-1}, 2000 \text{ cm}^{-1}]$ . This integrated amplitude response (or total scattered intensity, related to the reflectivity coefficient) is plotted as a function of distance from the space-exposed surface. Each scan is plotted using the same color scheme as in Figure 4. (Note: the shallowest point of scan 4 from sample 3 is beyond  $2 \mu\text{m}$ . As such, it is omitted from this figure.) Darkening occurs with greater proximity to the space-exposed surface in samples 2 and 3. Sample 1, which samples a hypervelocity impact crater on the same anorthite-rich plagioclase grain as samples 2 and 3, displays a shallower darkening trend than the other samples from 79221. There does not appear to be a strong correlation between depth and integrated amplitude response for sample 4. The dashed lines plotted for sections 1–3 are simple linear fits meant only to guide the eye.

344 scale mineralogical variations. The signal produced by diffraction-limited techniques is  
 345 an average over various mineral structures or compositions, making it unlikely that such  
 346 minor deviations in chemical composition would be detectable.

347 In samples 2 and 3, we observed reduced total scattered intensity with increasing  
 348 proximity to the space exposed surface (see Fig. 12). This darkening may be associated  
 349 with an increasing concentration of  $\text{npFe}^0$  near the surface (Noble et al., 2007; Lucey &  
 350 Riner, 2011). Surface-correlated amorphization may be a more parsimonious explana-  
 351 tion, however, since the host grain for samples 1–3 does not contain an appreciable amount  
 352 of iron. Suppose that the observed darkening results from the amorphous surface lay-  
 353 ers produced by long-term exposure to the space environment. In that case, it is plau-  
 354 sible that the hypervelocity impact (sample 1) vaporized or melted this layer; this could  
 355 explain why no darkening was observed for sample 1 despite originating from the same  
 356 soil grain as samples 2 and 3. This scenario is consistent with the widespread evidence  
 357 of impact-induced shock and vitrification seen near the crater in sample 1 (see Fig. 7).  
 358 Similarly, we did not observe a robust correlation between total scattered intensity and  
 359 depth for sample 4, suggesting that it contains limited concentrations of  $\text{npFe}^0$  or is oth-  
 360 erwise more robust to the space environment over the studied wavelength range.

361 However, it is important to note that samples 2 and 3 were extracted parallel to  
 362 one another and nearly perpendicular to section 1. As such, the effect of crystallographic  
 363 orientation cannot be ruled out when comparing results among the samples. The primary  
 364 observations —namely, that there is depth-dependent spectral variation between the grain  
 365 interior and the space-exposed surface —are not affected by this limitation.

366 Where present, the darkening effect is most apparent within 500 nm of the grain  
 367 surface (see Fig. 12). This depth falls just outside of the observed range of thicknesses  
 368 for amorphous rims in lunar soil ( $\sim 10$ – $350$  nm; Burgess and Stroud (2018); Christoffersen  
 369 et al. (1996)), but well within the range of thicknesses for glassy silicate layers ( $10$ – $1000$  nm)  
 370 thought to have been produced by micrometeoroid impacts (Noble et al., 2005). For com-  
 371 parison, the average implantation depth of solar wind-produced H and He has been es-  
 372 timated as  $\sim 20$ – $100$  nm (Christoffersen et al., 1996; Farrell et al., 2015; Tucker et al., 2019).

373 That we observed space weathering effects at depths greater than the penetration  
 374 range of typical solar wind protons could suggest that the implanted hydrogen diffused  
 375 into the grain. Although some diffusion undoubtedly occurs, it is unlikely to be the dom-  
 376 inant cause of the observed effects given the relatively poor H-retention of lunar soil (Farrell  
 377 et al., 2015). Alternatively, the effects observed could result from the occasional bom-  
 378 bombardment of the lunar surface by solar energetic particles (SEPs), which are substantially  
 379 more energetic than solar wind ions. Hydrogen SEPs have kinetic energies of  $2$ – $10$  MeV  
 380 (Mewaldt et al., 2009), whereas typical solar wind  $\text{H}^+$  ions have kinetic energies of  $\sim 1$  keV  
 381 (Gosling et al., 1976). Although SEPs are likely to implant further into lunar soil than  
 382 average solar wind ions, they occur far less frequently. Without additional support from  
 383 independent lines of evidence (e.g., observing tracks via TEM), these confounding fac-  
 384 tors preclude definitive conclusions about the role of SEPs in the weathering of our sam-  
 385 ples.

## 386 5 Conclusions

387 We used SINS to examine surface-correlated, mid-IR space weathering effects in  
 388 lunar soil grains. In general, our results are consistent with the spectral changes previ-  
 389 ously hypothesized to be correlated with the microstructural and compositional changes  
 390 measured by TEM. Crucially, however, our results demonstrate that SINS (and related  
 391 techniques) can be used to investigate the spatial scales over which ion irradiation and  
 392 micrometeoroid bombardment affect the soil’s optical properties. With a spatial reso-  
 393 lution comparable to the scale of space-weathering induced microstructural and chem-

394 ical changes, SINS can be used to establish a direct link to bulk space weathering effects.  
 395 As such, we have shown that this technique fills the gap between TEM microstructural  
 396 studies and far-field FTIR measurements.

397 The data presented above provide clear evidence supporting previous findings that  
 398 space weathering effects result from highly localized features (on the order of tens of nanome-  
 399 ters). We found that the effect size varies continuously (at the sampled spatial resolu-  
 400 tion) over a micrometer-scale range of depths. Our results additionally indicate that soil  
 401 maturity indices should be used with caution when discussing micron-scale sub-samples  
 402 of lunar soil. While the soil maturity index is a reliable predictor of large-scale weath-  
 403 ering effects, our results reinforce the variability of exposure history among a soil's con-  
 404 stituent grains.

405 The techniques utilized in this study have been shown to produce results similar  
 406 to those observed in bulk lunar soils. Taking advantage of techniques with spatial res-  
 407 olutions on the order of tens of nanometers, such as afforded by SINS, may prove use-  
 408 ful for studying the relative contribution of each small-scale process (e.g., solar wind im-  
 409 plantation, nano-phase iron production, micrometeoroid impacts) to the overarching space  
 410 weathering phenomenon. SINS data may also inform and refine the techniques used to  
 411 simulate weathering phenomena in the laboratory. With a more detailed understanding  
 412 of the spectral effects of charged-particle irradiation on mineral and soil grains, it may  
 413 also be possible to draw parallels to, inter alia, silicate processing in the interstellar medium  
 414 (Chiar & Tielens, 2006). Detailed studies of the association between specific molecular  
 415 vibrational modes and the features present in SINS spectra of minerals may shed fur-  
 416 ther light on various space weathering mechanisms. Information regarding the molecu-  
 417 lar bonds affected by space weathering, paired with precise chronometry and composi-  
 418 tional measurements of weathered lunar soils, may help to constrain or validate current  
 419 models of space weathering processes.

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## 427 Data Availability Statement:

428 The data used for this research is available at the Digital Research Material Repository  
 429 at Washington University in St. Louis (Utt et al., 2020).

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