Maskelynite Formation via Solid-State Transformation: Evidence of Infrared and X-Ray Anisotropy

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Abstract

We present optical microscopy, micro-Raman spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, high energy X-ray total scattering experiments, and micro-Fourier transform infrared (micro-FTIR) spectroscopy on shocked labradorite from the Lonar Crater, India. We show that maskelynite of shock class 2 is structurally more similar to fused glass than to crystalline plagioclase. However, there are slight but significant differences – preservation of original pre-impact igneous zoning, anisotropy at Infrared wavelengths, X-ray anisotropy,, and some intermediate range ordering – which are all consistent with a solid-state formation of maskelynite.

1. Introduction

Across the Solar System, impact cratering has played a major role in modifying the surfaces of planetary bodies. On the Earth, impact events are important for the evolution of the Earth's surface (e.g., the Chicxulub event at the end of the Cretaceous), but impacts are often obscured by other subsequent more active geologic processes such as plate tectonics, erosion, and deposition. For other planetary bodies such as Mars and the Moon, the lack of crustal recycling processes allows for greater preservation of the impact cratering record, leaving large expanses of heavily cratered terrain. This heavily cratered terrain is frequently the target of robotic missions, and the Opportunity Rover has already encountered material interpreted to be impact ejecta in Meridiani Planum (e.g. Bounce Rock). Additionally, many of the martian meteorites, particularly the shergottites, show evidence of moderate to high shock. Therefore correctly interpreting the geologic histories of these planetary bodies requires a full understanding of the crystallographic and structural changes due to shock. Specifically, we investigate the structural differences between plagioclase and maskelynite because maskelynite is a major component of

lunar and martian crustal rocks. In this paper, first we describe the structure of maskelynite and compare it to that of crystalline plagioclase and fused plagioclase-composition glass, then we discuss possible formation mechanism and conditions.

2. Background

2.1 Shock Metamorphism

A hypervelocity impact event results in the generation of a shock wave traveling through both the target and the impactor. As a result, the impactor is obliterated through melting and/or vaporization and the target rocks undergo a progression of deformation effects [Short and French, 1968; Stöffler, 1971; Melosh, 1989; Osinski and Pierazzo, 2013 and refs therein]. Collectively referred to as impact metamorphism, these effects include brecciation, large scale mechanical mixing of target components, structurally controlled planar deformation features (PDFs), solid-state mineral transformations, formation of high-pressure mineral polymorphs, melting, geochemical mixing of target components, and vaporization of the target and/or impactor [Chao, 1968; von Englehardt and Stöfffler, 1968; French and Koeberl, 2010; Osinski and Pierazzo, 2013, and refs within]. A subset of these effects – solid-state internal chemical and structural changes linked directly to the shock wave, i.e. "shock metamorphism" – have received special attention as they are unique to shock and cannot be produced by non-impact processes [Alexopoulos et al., 1988; Langenhorst, 2002; Ferrière and Osinski., 2013].

On the Earth, the majority of studies of shock metamorphism have focused on the mineralogic changes in tectosilicates, specifically quartz and feldspar, which have crystal structures more susceptible to shock deformation than other silicate types [Stöffler et al., 1991; Johnson et al., 2002; Langenhorst, 2002]. Shock effects in other minerals, such as zircon [Bohor et al., 1993; Wittmann et al., 2006] and olivine [Stöffler et al., 1991; Van de Moortèle et al., 2007] are known

58 to occur, but these have been less extensively studied because planar deformation features in
59 zircon have only recently been discovered, and shocked olivine has only been documented in
60 meteorites and has yet to be reported in terrestrial impactites [Stöffler et al., 1991].
61 For extraterrestrial materials, shock effects in plagioclase are most relevant for studies of
62 basaltic or anorthositic surfaces, which commonly occur on Mars and the Moon. Shock effects in
63 plagioclase, while less commonly studied than shock effects in quartz, have been well
64 documented from both natural and experimental impacts [Chao, 1968; von Englehardt and
65 Stöffler, 1968; Stöffler, 1971, 1972; Hörz and Quade, 1973; Reimold 1982; Ostertag, 1983;
66 Heymann and Hörz, 1990; Johnson et al., 2002, 2003; Fritz et al.. 2005; Johnson, 2012; Jaret et
67 al.,2014; Pickersgill et al., 2014]. Shock effects in plagioclase represent a progression of
68 deformation and show continued degradation of the crystal lattice with increasing shock pressure
69 [Stöffler, 1971; Kieffer et al, 1976; Hanss et al., 1978; Ostertag, 1983; Heyman and Hörz, 1990;
70 Stöffler et al., 1991; Fritz et al., 2005, Johnson et al., 2012]. A major change in plagioclase
71 crystal structure occurs at shock pressures of ~28-34 GPa, at which point it transforms to a
72 diaplectic glass, referred to as maskelynite [Bunch et al., 1967; Ostertag, 1983]. Interestingly, the
73 transition to maskelynite is gradational and highly variable depending on specific pre-shock rock
74 properties (e.g., composition, grain size, porosity, etc) and in some cases plagioclase can retain
75 partial crystallinity up to ~45 GPa [Ostertag, 1983].
76 This transformation and loss of crystallinity is a major transition resolvable optically and
77 spectroscopically, that marks an important change in response to shock of plagioclase. Thus, this
78 process has been the focus of intense research for nearly 60 years [Milton and DeCarli, 1963;
79 Bunch et al., 1967; Stöffler, 1971; Hörz and Quade, 1973; Bischoff, and Stöffler, 1984; Ostertag,
80 1983; Chen and El Goresy, 2000; Fritz et al. 2005; El Goresy et al., 2013].

81 *2.2 Maskelynite Formation*

82 Despite multiple studies of maskelynite, there has been considerable debate over its formation
83 mechanism. Much of the debate over maskelynite formation centers around whether or not it
84 forms via solid-state deformation as a diaplectic glass [Bunch et al., 1967; von Englhardt and
85 Stöffler., 1968; Hörz and Quade, 1973], after shear induced melting [Grady, 1980], or is
86 quenched as a fused glass under high pressure [Chen and El Goresy, 2000]. Solid-state and
87 melting-related formation mechanisms are distinct processes and have different implications for
88 the geochemical behavior of the rock during impact deformation. Most importantly for
89 understanding geochronology, melting and quenching of a fused glass would produce a new
90 material whose age would reflect the time of impact. However, a solid-state mechanism for
91 maskelynite formation need not necessarily reset isotope systems. Unfortunately, nomenclature
92 is muddled in the literature with maskelynite and diaplectic glass often used interchangeably
93 [Tschermak, 1882; Bunch et al., 1967; Stöffler, 1971; Arndt et al., 1982; Ashworth and
94 Schneider, 1985; White, 1993; Chen and El Goresy, 2000].

95 Even within these two genetic models (melt vs. solid state), the exact formation mechanism is
96 unclear. Multiple hypothesis have been proposed. Solid-state models (aka. diaplectic glass
97 models) include: (1) reversion of high pressure phases to glass [Ahrens et al., 1969; Williams
98 and Jeanloz, 1988]; (2) metamict-like destruction of the unit cell [Ashworth and Schneider,
99 1985]; and (3) pressure-induced formation of high coordination glasses [Hemley, et al., 1988].

100 Models involving melting include: (4) shear-band induced melting [Grady et al., 1980; Grady
101 et al., 1997] and (5) quenching of dense melt under high pressure [Chen and El Goresy, 2000].
102 Although these models have all been applied to plagioclase [White, 1993], many of the diaplectic
103 glass models, such as formation of high coordination glass [Ahrens et al., 1969] and metamict-

like disruption of the structure at the unit cell scale [Ashworth and Schneider, 1985], are based on SiO_2 with the assumption that framework silicates behave similarly. Only a few studies [Hörz and Quade, 1973, Arndt et al., 1982; Diemann and Arndt, 1984; White 1993] have specifically focused on plagioclase. Given the additional structural and chemical complexity of the feldspar system compared to SiO_2, more work focused specifically on this system is warranted.

Previously, a number of analytical and spectroscopic methods have been applied to investigate the structure of maskelynite and other shocked mineral in order to better infer the formation process. This paper presents an integrated approach which combines multiple analytical results of the same samples.

2.3 Optical Petrography

Maskelynite, initially identified in the martian basaltic meteorite Shergotty [Tschermak, 1872] was first described as optically isotropic material derived from plagioclase [Milton and DiCarli, 1963; Bunch et al., 1976; Stöffler, 1972]. Petrographically, maskelynite appears similar to plagioclase in plane-polarized light, preserving grain boundaries and texture of the target rock, but has a lower refractive index than unshocked plagioclase. In cross-polarized light, however, maskelynite is easily distinguished from unshocked plagioclase as it is optically isotropic (e.g., Figure 1).

2.4 Raman Spectroscopy

Raman Spectroscopy, a vibrational spectroscopic technique that relies on inelastic scattering, is sensitive to low-frequency lattice modes, and is therefore useful for probing mineral crystal structures. As Raman spectroscopy is sensitive to crystallinity, it has been used previously to distinguish and characterize shocked feldspars [Veld and Boyer, 1985; Chen and El Goresy, 2000; Fritz et al., 2005; Jaret et al., 2014].

127 Crystalline plagioclase has several well defined Raman active vibrational modes: cation and
128 lattice modes occurring between 200 and 400 cm^{-1}, symmetric T-O-T stretching modes occurring
129 between 500 and 600 cm^{-1}, asymmetric O-T-O bending modes occurring between 600 and 700
130 cm^{-1}, T-T stretching modes occurring between 700 and 800 cm^{-1}, and T-O stretching modes
131 occurring between 1050 and 1150 cm^{-1} [see Sharma, 1983 for complete band assignments]. It
132 should be noted that the exact position of these peaks can vary with composition due to the solid-
133 solution within the plagioclase series [Mernagh, 1991; Freeman et al., 2008]. Specifically the
134 strongest and most diagnostic peaks occur at 509 cm^{-1}, 485 cm^{-1}, at 1030 cm^{-1}. These three peaks
135 are useful both for identification of specific feldspar composition [Freeman et al., 2008], and for
136 assessing the level of shock as shown by the decrease in intensity ratio of the 485:509 peaks,
137 merger of these peaks, and significant broadening of the 1030 cm^{-1} peak [Fritz et al., 2005].

138 *2.5 Nuclear magnetic resonance (NMR) spectroscopy*

139 Solid-state nuclear magnetic resonance spectroscopy observes nuclear spin transitions as a
140 way of characterizing local chemical environment. This technique is particularly useful for
141 analysis of amorphous material because it is sensitive only to local environment and not long-
142 range order. Specifically, the position of a peak's chemical shift is representative of the number
143 and length of Si-O bonds and the next nearest neighbor atoms. The peak width provides a
144 measure of disorder, and the area under the peak is proportional to the number of nuclei in that
145 local environment. In silicates, the chemical shift is most strongly affected by cation-oxygen
146 distances. Increasing the coordination number (i.e., increasing the mean cation-oxygen distance)
147 generally corresponds to decreasing the chemical shift [Phillips, 2000; Stebbins and Xue, 2014
148 and refs within]. Thus, NMR spectroscopy can be a particularly useful tool for studying shocked

149 material since changes in cation-oxygen distances, increasing coordination number of cations,
150 order/disorder, and the formation of glasses all can occur in response to impact events

151 NMR spectroscopy of shocked minerals has largely been limited to SiO_2 [Yang et al., 1986;
152 Fiske et al., 1998; Boslough et al., 1995; Lee et al., 2012]. Few studies have considered feldspar,
153 and these have been primarily focused on the low-shock regime, at pressures below the transition
154 to maskelynite [Cygan et al, 1991], and show that up to ~25 GPa shock pressures no systematic
155 changes to Si or Al coordination can be detected.

156 *2.6 X-ray Scattering*

157 Numerous X-ray diffraction studies have been conducted on shocked tectosilicates [Hanss et
158 al., 1978; Arndt et al., 1982; Ostertag, 1983; Diemann and Arndt, 1984]. These studies show that
159 for both naturally and experimentally shocked samples the silicate structure collapses with
160 impact pressure [Hörz and Quade, 1973; Pickersgill et al., 2014]. Both Debye-Scherrer
161 (powders) and target micro-XRD measurements of individual grains show that increasing shock
162 level corresponds to increased asterism and streaking along Debye rings [Hörz and Quade, 1973;
163 Pickersgill et al., 2014]. This breakdown of the crystal lattice is progressive, and strongly
164 correlates with shock pressure, and XRD has been suggested as a tool for quantifying shock
165 pressures analytically [Hörz and Quade, 1973; Pickersgill et al., 2014].

166 In one of the only X-ray structural studies of shocked feldspar, Diemann and Arndt, [1982],
167 compared diaplectic glass from the Manicuagan impact structure to a fused glass (at atmospheric
168 pressure) of similar composition. They showed that there is little structural difference between
169 the fused glass and diaplectic glass. However, they also state that in some cases the diaplectic
170 glass may be slightly less disordered than fused glass. They interpret this to reflect “relics” of
171 crystalline plagioclase preserving long-range order of its former pre-shock state, as in the shock

transformation model of Grady [1980]. Alternatively, this could reflect an incomplete transformation to diaplectic glass, which is commonly seen optically at Manicouagan [Thompson, 2014].

2.7 Infrared Spectroscopy

Infrared spectroscopy is a particularly useful tool for mineral identification, as the positions and strengths of bands are related to the specific vibrational modes of mineral crystal lattices. Feldspar minerals have absorption bands between 450 and 1200 cm^{-1} reflecting vibrations of $(Si,Al)O_4$ tetrahedra [Iiishii, et al., 1971]. Bending vibrations in the Si-O-Al planar ring occur between 400 and 550 cm^{-1}. Octahedral stretching of SiO_6 occurs between 750 and 850 cm^{-1}, and as minor features between 450 and 700 cm^{-1}. Asymmetric stretching of Si-O occurs between 900 and 1200 cm^{-1}. Contributions from Na-O and Ca-O vibrational modes occur below 450 cm^{-1} [Iiishii et al., 1971; Johnson et al., 2003].

Shock metamorphism, which can cause changes to the refractive index, bond length, and cation coordination number, can cause measureable changes to a mineral's infrared spectrum. For feldspar minerals, Bunch et al. [1967] showed that increasing shock corresponds to decreasing spectral detail and decreasing intensity of absorption features. Stöffler [1972] and Stöffler and Hornemann [1972] showed decreases in absorption features with increased shock pressure, but also showed that band positions shift to lower wavenumbers with increased shock. These shifts are believed to be due to the initial formation of amorphous material at about 20 GPa [Stöffler, 1972; Johnson et al., 2003].

3. Samples and Methods

3.1 Samples

194 The samples used in this study were collected at the Lonar crater in 2005 (S. Wright). The
195 Lonar Crater, India is a rare terrestrial impact site, as it is the only terrestrial impact (of ~190
196 known) emplaced entirely into flood basalt target rocks (Earth Impact Database, 2011, available
197 at http://www.passc.net/EarthImpactDatabase/index.html). The target lithology is a series of
198 basalt flows, ranging in thickness from 5 to 30 m. Only minor petrographic differences
199 (specifically the number and size of phenocrysts) occur between flows. Texturally, these rocks
200 contain labradorite phenocrysts up to 2 mm in diameter in a fine grained groundmass (~0.2 mm).
201 Compositionally, these rocks are dominated by labradorite (An_{65}), augite, pigeonite, and iron-
202 titanium oxides [Kieffer et al., 1976; Wright et al., 2011]. Shocked samples for this study consist
203 of Class 2 basalt ("LC09-253," see [Wright et al., 2011]), which was a clast within the proximal
204 ejecta blanket. For comparison to crystalline labradorite, we used samples from Ajanta ("AJ-
205 101"), collected from the Deccan flows, but away from the crater proper [Wright et al., 2011].
206 For comparison with fused glass we used synthetic labradorite glass (An_{63}).
207 *3.2 Methods*
208 For comparison to maskelynite and unshocked labradorite, we synthesized fused glass of
209 labradorite composition. We separated labradorite grains from unshocked Decaan basalts (from
210 Ajanta, India, see Wright et al., [2011] with the Selfrag electromagnetic separator to insure a
211 pure starting material. A total of 100 mg of separated labradorite grains were heated in a Deltec
212 furnace to 1500°C in a sealed Pt crucible for 90 minutes and quenched.
213 We conducted optical petrography on polished thin sections. NMR spectroscopy and X-ray
214 total scattering experiments were conducted on powders and of single grains of separated
215 maskelynite grains. Micro-FTIR spectroscopy measurements were conducted on oriented single

grains. Individual grains were separated using the Selfrag electro-magnetic separator at the Lamont Dougherty Earth Observatory and then hand-picked under binocular microscopes.

For our electron probe microanaysis, we used the JEOL JXA-8200 Superprobe in the Department of Earth and Planetary Sciences at Rutgers University. Standards included Great Sitkin USNM 137041 Anorthite, Kakanui 133868 anorthoclase, NMNH 143966 Microcline, Lake County USNM 115900 plagioclase, Tiburon albite, and Kakanui for Fe. All analyses used 15 kEv, 15nA, and a 1 micron spot size, with time dependent integration correction to prevent loss of K and Na.

We collected micro-Raman spectra using a WiTec alpha300R confocal imaging system, equipped with 532 nm Nd YAG laser with 50 mW nominal power at the sample surface, and a spot size of 0.76 μm. Each spectrum was acquired through a 50X (0.85 NA) objective, and consisted of 60 acquisitions each with a 1 second integration time. All measurements used standard thickness polished thin sections.

We acquired NMR spectra for ~10 mg of separated maskelynite grains and a sample of crystalline labradorite of similar composition. The ^{29}Si spectra were obtained at 9.4 T and 10 kHz spinning rate, and ^{27}Al and ^{23}Na spectra at 11.7 T with a 20 kHz spinning rate.

High energy X-ray total scattering experiments used 10 mg of picked maskelynite grains, fused glass of labradorite composition as well as maskelynite grains in different orientations. Two dimensional diffraction data were collected on a Perkin-Elmer XRD 1621 detector at the beamlines 11-ID-B at the Advanced Photon Source (APS) and X17B3 at the National Synchrotron Light Source (NSLS) with a wavelength of 0.2128 Å and 0.1529 Å, respectively. The background from the Kapton capillary and the hutch were measured and subtracted from the exposures containing the sample. Fit2D was used for the determination of the geometric

239 parameters and the radial integration of the two-dimensional data [Hammersley et al., 1996]. The
240 total scattering function $S(Q)$ was obtained using the program PDFgetX2 [Qiu et al., 2004] where
241 standard corrections were applied as well as those unique to area-detector geometry [Chupas et
242 al., 2003]. The pair distribution function $G(r)$ was generated by direct Fourier transformation of
243 $S(Q)$ with a Q_{max} of 22 Ä$^{-1}$.

244 We collected Micro-FTIR point spectra of single grains in thin section using a Nicolet
245 iN10MX FTIR microscope, in the Vibrational Spectroscopy Laboratory at Stony Brook
246 University. This instrument is equipped with a liquid nitrogen-cooled HgCdTe array detector
247 capable of acquiring hyperspectral image cubes between 715 and 7000 cm^{-1} (1.4-14 µm) at 25
248 µm/pixel spatial sampling. To test for spectral isotropy of single grains of maskelynite were
249 individually mounted in an epoxy puck, and the single grain was then rotated 90 degrees to
250 obtain measurements of multiple orientations through the grain. This was repeated with 3
251 different grains.. Similar method was used for crystalline labradorite and fused glass.

252 4. Results

253 *4.1 Optical Petrography*

254 In plane-polarized light, Lonar maskelynite occurs as phenocrysts and within the groundmass.
255 Maskelynite appears uniformly smooth, lacking planar deformation features (PDFs), and planar
256 fractures (PFs). Both phenocrysts and grains within the groundmass are euhedral to subhedral
257 and show no textural evidence of melting (Figure 1A). In cross-polarized light, maskelynite
258 grains remain at extinction through complete 360 degree rotation of the microscope stage
259 (Figure1B-E). No remnant or partial birefringence was observed. Pyroxenes, however appear
260 unaffected by shock, showing typical interference colors, and lack fracturing or granularization
261 commonly reported for highly shocked basalts.

Based on optical shock classification schemes, these samples are low to moderate shock, Class 2 [Kieffer et al., 1976] or Stage I [Stöffler, 1971], indicating shock pressures between 25 and 28 GPa, as suggested by only minor cracking of adjacent pyroxenes [Kieffer et al., 1976; Stöffler, 1971].

4.2 MicroRaman Spectroscopy

As shown in figure 2, unshocked labradorite exhibits characteristic peaks at 190, 482, 505, 561 cm^{-1} and lower intensity peaks at 270, 406, 778 cm^{-1} and a slight peak centered near 1030 cm^{-1}. Fused labradorite glass exhibits two broad peak 495 and 1025 cm^{-1}, with FWHM of 169 and 138 cm^{-1} respectively. There is also a slight shoulder at 559 cm^{-1}. Maskelynite also exhibits two broad peak 482 and 1012 cm^{-1}, with FWHM of 174 and 189 cm^{-1} respectively. There is also a slight shoulder at 559 cm^{-1}.

4.3 NMR Spectroscopy

NMR spectra and peak perameters for ^{29}Si, ^{27}Al, and ^{23}Na are shown in Table 2. The NMR spectra of Lonar maskelynite contain broad, featureless peaks indicative of extensive short-range disorder beyond the first coordination sphere. For example, the ^{29}Si spectrum (Figure. 3A), shows a broad, approximately Gaussian-shaped peak for 4-coordinated Si centered near -91 ppm with a width of 18.6 ppm FWHM. In comparison, the spectrum of crystalline, unshocked labradorite is asymmetric and contains fine structure from resolution of distinct crystallographic sites and local environments with differing numbers of adjacent framework Al atoms, typical for intermediate composition plagioclase feldspars [Kirkpatrick et al. 1985]. Fused glass is slightly broader (3 ppm) than maskelynite and the peak position is also shifted to a more negative chemical shift by 3 ppm.

^{27}Al results show maskelynite has a peak centered at 52.7 ppm and a FWHM of 36.5 ppm. Fused glass has a peak centered at 53.3 ppm and FWHM of 31.2 (Fig. 3B).

^{23}Na results show maskelynite has a peak center at -18.6 ppm and FWHM of 25.0 ppm. Fused glass has a peak centered at -19.7 and FWHM of 24.3. (Fig. 3C).

4.3 High Energy X-ray Total Scattering

The structure factor *S(Q)* of the different maskelynite grains and the fused glass, and multiple maskelynite grains in a capillary are shown in figure 4. On basis of the structure factor, the samples of single maskelynite and fused glass grains are indistinguishable, while the assortment of grains in the capillary show signs of some crystalline contribution. The minor crystalline phase in the capillary data was identified as plagioclase, suggesting that some or parts of the separated grains were crystalline plagioclase. The pair distribution functions *G(r)*, of the maskelynite grains and fused glass are shown in figure 5. The largest correlations observed in the *G(r)* for all investigated samples are less than 10 Å, similar to the unit cell parameters for one unit cell in plagioclase [Wenk et al, 1980]. Therefore, it can be concluded that maskelynite is an amorphous solid and not nanocrystalline. The local region of the pair distribution function of maskelynite samples and the fused glass are similar. All show the characteristic maximum at 1.6 Å and 3 Å characteristic for Si-O distances in tetrahedral and the inter-tetrahedral Si-Si distance. The Si-Si distance in maskelynite and the fused glass is shorter than the Si-Si distances in crystalline labradorite [Wenk et al, 1980] indicating a modification or break-up of the ordered tetrahedral crankshaft structure in crystalline plagioclase. The range in the pair distribution function between 4 and 10 Å allows insight into the connectivity of the local structure motive. Here, a significant difference of the intermediate range order can be observed between the maskelynite samples and the fused glass (inset figure 5). The two maskelynite grains show more

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resolved maxima in the intermediate range in the G*(r)*, compared with the *G(r)* of the fused glass, suggesting a higher degree of intermediate range order in the maskelynite.

Figure 6 shows the *G(r)* of maskelynite grain 1 collected at different orientation randomly, rotated 90° from the first. The pair distribution function *G(r)* is distinctively different between the two orientations, potentially showing a remnant of anisotropy otherwise only observed in crystalline samples.

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4.4 Micro-FTIR Spectroscopy

Unshocked labradorite exhibits 2 primary peaks, dependent upon orientation. The first peak is centered at 900 or 1001 cm^{-1}, and the second peak is centered between 1100 and 1175 cm^{-1}. However, at some orientations, a small shoulder also develops near 990 cm^{-1} in addition to a peak near 900 cm^{-1}, (Fig. 7A). The fused glass of labradorite composition exhibits one peak centered at 995 cm^{-1}, the position of which is independent of orientation (Fig. 7B).

Maskelynite exhibits one broad peak compared to two narrower peaks typical of crystalline labradorite. The peak position varies by nearly 40 cm^{-1} depending upon orientation. For orientation 1, the peak position was centered at 960 cm^{-1}, whereas after being rotated to an orientation perpendicular to the first measurement, the peak position is centered at 1000 cm^{-1} (Fig. 7C).

5. Discussion

5.1 Comparison of maskelynite to fused glass and crystalline labradorite

Our results highlight the importance of a multi-technique approach. Only using one technique – particularly either Raman or Infrared spectroscopy – may be insufficient to properly distinguish crystalline plagioclase, maskelynite and fused plagioclase-composition glass.

330 Raman spectroscopy reveals that maskelynite is distinctly different from the crystalline
331 labradorite, with a spectrum nearly identical to that of fused glass (figure 2). There are slight
332 differences between the maskelynite and the fused glass in both peak position and intensity.
333 Fused glass shows a higher intensity of the 495 cm^{-1} peak compared to the background.
334 However, this is minor and likely reflects nonstructural differences such as quality of the surface
335 polish. The position of the fused glass and maskelynite peaks are offset from one another, but
336 given the broad nature of these peaks, this difference in peak center is not considered substantial
337 enough to be indicative of compositional or structural difference. This pattern of two broad peaks
338 centered near 495 cm^{-1} and 1025 cm^{-1} is also consistent with Raman patterns of synthetic fused
339 glass of various plagioclase compositions [Sharma et al., 1983]. In agreement Trieman and
340 Treado [1998], Raman spectroscopy alone is not sufficient for distinguishing impact melt-glass
341 (i.e., fused glass) from maskelynite. This is important because Raman spectroscopy has been
342 used to identify and distinguish maskelynite from fused glass [Chen and El Goresy, 2000].
343 NMR results for ^{29}Si show that both fused glass and maskelynite have just one symmetric
344 peak rather than an asymmetric partially resolved spectrum typical of crystalline labradorite
345 (figure 3). Both fused glass and maskelynite are shifted towards more negative chemical shifts
346 indicating loss of short-range order. Fused glass and maskelynite are also different from each
347 other with fused glass being 3ppm broader than maskelynite and the peak position is also shifted
348 to a more negative chemical shift by 3 ppm. These differences between maskelynite and fused
349 glass likely reflect differences in formation mechanism. It is possible that composition and
350 quenching rate can affect peak width and position, but here the maskelynite and fused glass are
351 compositionally similar (An_{60} vs An_{63}) and quenching was done very rapidly. We suggest that

352 these differences between fused glass and maskelynite, while minor, are reflecting differences in
353 structural order.
354 Recently, Lee et al. [2012] showed NMR evidence for shock-induced changes to Al
355 coordination in experimentally shocked fused glasses. They showed that after shock the ^{27}Al
356 peak center moves to a more negative chemical shift and the peak width increases and is
357 associated with small amounts of higher coordination Al. Our maskelynite does show some six-
358 coordinated Al, reflecting a minor clay component, which is not unlikely for weathered
359 plagioclase. Our NMR results are consistent with any of the solid state deformation models..
360 The X-ray total scattering data show similarity on the length scale of the local structure
361 between fused glass and maskelynite (figure 4). Here, we compared maskelynite of An_{63}
362 composition to fused glass of pure anorthite composition. Despite the compositional differences,
363 there is no detectable difference in *S(Q)* between the fused glass and the maskelynite.
364 However, ~~a~~ significant differences ~~is~~ are observed in the intermediate range of the pair
365 distribution function *G(r)* between fused glass and maskelynite. Maskelynite shows a higher
366 degree of intermediate range order compared with fused glass (figure 5-6).
367 Furthermore, the residual anisotropy in the atomic arrangement of maskelynite observed in
368 the *G(r)* of the same maskelynite grain in different orientation suggests that maskelynite is not
369 formed through a melting process but rather through a direct amorphization from a crystalline
370 phase.
371 Infrared spectra of unshocked labradorite show strong peaks at 1140 and 950 cm^{-1}
372 corresponding to the Si-O stretching and (Si,Al)-O stretching modes respectively [Iiishi et al.,
373 1971].

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374 Although these maskelynite grains are optically isotropic at visible wavelenghts, the
375 orientation-dependent infrared reflectance peak position shifts (Fig. 7) suggests the maskelynite
376 is not isotropic in the infrared. We replicated the IR experiments for 3 individual grains and the
377 results shown in figure 7 represent the largest difference in peak positions of the 3 grains. The
378 value of this shifting can vary depending on the exact orientations being measured and
379 unfortunately, we are unable to determine exactly which crystallographic axes our measurements
380 were taken along.
381 Our analyses suggest that shock produced maskelynite "glass" is fundamentally different
382 from fused glass because fused glass does not show any effect of orientation. For maskelynite,
383 we suggest these grains formed by short-range atomic displacements rather than melting without
384 internal homogenization resulting from long-range or diffusive movement of atoms within the
385 grain. Such a formation mechanism is consistent with the observed preservation of grain
386 boundaries and zoning of the maskelynite and lack of flow textures, suggesting a formation
387 mechanism purely via solid-state transformation [Stöffler, 1971; Hörz and Quade, 1973] not
388 through quenching of a higher pressure melted glass [Chen and El Goresy, 2000; El Goresy et
389 al., 2013]).
390 Previous infrared studies of maskelynite [Ostertag, 1983; Johnson et al., 2003] showed that
391 spectrum maskelynite was indistinguishable from the spectrum of fused glass. These studies
392 differ from ours in that they measured powders of larger samples which included multiple grains
393 rather than individual grains, resulting in averaging orientation in the spectra. By measuring
394 multiple orientations of singe grains, we show that that maskelynite is amorphous yet not
395 necessarily isotropic at all wavelengths.

The cause of anisotropy of maskelynite at infrared but not at visible wavelengths remains somewhat perplexing, but we offer two possible explanations. First, this could be due to a difference in sensitivity of the instruments – traditional polarizing light microscope and human eyes for visible light versus an HgCdTe array detector for the IR. Perhaps the IR detector is simply more sensitive and is able to detect changes that are not resolvable with our eyes. Alternatively, this anisotropy could be related to how the shock process affects the refractive index during transformation from plagioclase to maskelynite. In visible light, the maximum difference in refractive index with orientation is small compared to that at IR wavelengths. Perhaps, during maskelynite formation, the difference in refractive index is decreasing such that at visible wavelengths there is not a detectable difference but at IR, which started out large, still retains a detectable difference with orientation.

Anisotropy at X-ray wavelengths is easier to explain. We attribute this to maskelynite formation by short-range atomic displacements, leaving some of the atomic-scale feldspar topology mostly intact. Unlike the visible and IR anisotropy, our X-ray analyses do not rely on reflectance and probe the atomic structure directly.

Our X-ray results are different from previous X-Ray studies, which used powders [Ostertag, 1983], or unoriented micro-XRD [Pickersgill et al., 2014]. Neither technique would be capable of detecting anisotropy.

Importantly, these maskelynite grains in this study also show the preservation of original igneous crystallization textures, as illustrated by the preservation of oscillatory zoning (Figure 8). This is a remnant of pre-shock texture and the preservation of feldspar stoichiometry (Table 2) suggests that the transformation from labradorite to maskelynite was not accompanied by geochemical changes or diffusive loss of light elements such as Ca, Na, and K.

419 Zoning in terrestrial maskelynite has only been briefly noted from Lonar [Fredriksson et al.,
420 1979]. Martian maskelynite, on the other hand, has received considerably more discussion.
421 Zoning from $An_{54}Ab_{44}Or_2$ to $An_{42}Ab_{54}Or_4$ has been reported in Shergotty and nearly identical
422 $An_{55}Ab_{43}Or_2$ to $An_{43}Ab_{53}Or_4$ is seen in Zagami, and maskelynite from EETA 79001 shows
423 oscillatory zoning [Trieman and Treado 1998; Milkouchi et al., 1999]. Such preservation of
424 zoning has been used to argue that this meteoritic maskelynite formed via solid-state processes.
425 Similarly, we find it difficult to envision a scenario where melting would preserve this texture
426 because of likelihood of cations, especially Na, diffusing during melting and subsequent cooling.
427 The use of zoning in maskelynite as an indicator of solid-state deformation has been
428 challenged by Chen and El Goresy [2000], who claim that zoning in Shergotty maskelynite is
429 restricted to partially birefringent grains and those with Raman patterns indicative of crystalline
430 (or partially crystalline) material and that the zoning in Shergotty maskelynite reflects a region of
431 the sample that has not experiences as high shock. However, this is not the case for our samples,
432 as the same sample that exhibits preserved zoning has a Raman pattern consistent with an
433 amorphous material (figure 2).
434 *5.2 Formation mechanisms and conditions*
435 Three specific models of solid-state formation of pressure induced diaplectic glasses of
436 silicate composition have been proposed: (1) reversion of high pressure phases to glass [Ahrens
437 et al., 1969]; (2) metamict-like dissordering of the structure at the unit cell scale by short-range
438 atomic displacements [Ashworth and Schneider, 1985]; and (3) pressure-induced formation of
439 high coordination glasses [Bunch et al., 1967; Hemley, et al., 1988]. Our results are consistent
440 with any of these models. Even though we do not currently see high coordinated Si in these
441 samples, the static compression experiments of Williams and Jeanloz [1988] indicates that these

high coordination Si and Al revert back to four-fold coordination upon decompression, and thus would not be expected to be remaining in our samples.

While our data does not allow us to definitively favor any model, the metamict-like disordering model [Ashworth and Schneider, 1985] is particularly attractive as it provides both conditions under which the deformation occurs and provides a specific mechanism by which the deformation occurs. In their model for the quartz-diaplectic silica transformation, the shock wave is deforming the crystal lattice in the same manner as alpha particles do when they induce atomic displacements due to elastic collisions [Tomasic et al., 2008]. Perhaps an analogous process is occurring during the plagioclase-diaplectic plagioclase-composition glass transformation. Furthermore, annealing of metamict silicates leads to recrystallization and recovery of original structure [Tomasic et al., 1987; Berrau, 2012;], a property that also occurs in shocked diaplectic plagioclase-composition glasses.

Critically, it has been well established that shock effects in plagioclase are progressive [Stöffler, 1971; White, 1993; Fritz et al., 2005; Jaret et al., 2014] and our conclusions are only valid for maskelynite of moderate-level shock classes. As demonstrated previously [Kitamura et al., 1977; White, 1993; Pickersgill et al, 2014] multiple types of maskelynite occur, such as the PDF-type glass confined to planar crystallographically controlled orientations, whole-grain maskelynite with preserved texture, and an intermingling of these two types. This Lonar maskelynite only exhibits whole-grain type maskelynite and therefore we favor solid-state mechanisms for its formation, while other mechanisms such as the shear band model [Grady, 1977] may be applicable to other varieties of shocked feldspar [White, 1993; Kitamura et al., 1977].

464 It is highly likely that the preservation of anisotropy within maskelynite occurs at moderate
465 shock pressures just above the plagioclase-maskelynite transition. Based on petrography, this
466 sample is a Class 2 basalt [Kieffer et al., 1976] with estimated shock pressures of (~25 – ~28
467 GPa). Although the maskelynite is fully optically isotropic, the pyroxenes remain birefringent
468 (Fig. 1), suggesting that the overall shock level was moderate in this sample. Perhaps, at higher
469 shock levels, the structure of maskelynite may breakdown entirely, and it would lose any
470 remaining anisotropy. The two competing hypotheses for maskelynite formation may in fact be
471 due simply to the progressive nature of shock and maskelynite formation at multiple levels of
472 shock deformation.

473 *6. Conclusions*

474 We show that maskelynite formed at moderate shock level is the product of solid-state
475 transformation and did not form through melting or quenching. Although maskelynite is
476 optically isotropic and has Raman spectra identical to fused glass, X-ray total scattering data
477 show a higher degree of intermediate range order and anisotropy in maskelynite. Additionally,
478 infrared spectroscopy show differences reflecting preserved orientation effects. Similarly,
479 preservation of stoichiometric zoning within the maskelynite suggests minimal, if any, effect of
480 heat during transformation to maskelynite. We favor a maskelynite formation mechanism that is
481 purely solid-state, such as the mechanical disaggregation of the crystal lattice [Hörz and Quade,
482 1973; Arndt et al., 1982] most likely by metamict-like destruction [Ashworth and Schnieder,
483 1985].

484 This study also presents the first spectroscopic technique to distinguish shock-produced glass
485 from thermally produced glass, which not only has implications for the formation mechanism of
486 maskelynite, but also for planetary remote sensing. For planetary remote sensing, our work may

shed light onto the problem of distinguishing shock-glasses from other amorphous materials, particularly on Mars. Recently, X-ray diffraction onboard the Mars Curiosity Rover has found abundant amorphous material and there is considerable debate as to whether this material represents volcanic glass, highly weathered silica coatings, or shocked material from impact craters [Bish et al., 2013]. Since we cannot distinguish shock-produced solid-state glass from fused glass via unoriented methods such as powder X-ray diffraction, like that onboard Curiosity, shock processes cannot be ruled out as an explanation for amorphous material detected remotely on Mars.

Acknowledgements:

SJJ is supported by NASA Earth and Space Science Fellowship.

We thank Don H. Lindsley (SBU) for assistance with fused glass synthesis and Christopher Vidito (Rutgers) for assistance with the electron microprobe.

Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

The operation of the beamline X17B3 is partially supported by COMPRES, the Consortium for Materials Properties Research in Earth Sciences under NSF Cooperative Agreement EAR 11-57758

This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

This manuscript was greatly improved through conversations and discussion with Dr. Jessica Arnold, and XXX, YYY.

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759 Figure 1: Shocked basalt in thin section.

760 A) Plane polarized light, showing that the maskelynite (labeled M) and pyroxenes (labeled pyx).

761 B-E) cross-polarized light images of the same location of the thin section as A, taken at 90-
762 degree rotations of the microscopy stage. Specific stage orientations shown in the inset. This
763 sample is thus a low-to-moderately shocked sample (Class 2) according to the shock
764 classification scheme of Kieffer et al. [1976]. Importantly, maskelynite is fully isotropic but no
765 changes are seen in pyroxenes.

766

767 Figure 2: Micro-Raman spectra of unshocked labradorite (upper line, blue), fused glass (middle
768 line, red), and maskelynite (lower line, green). Only the unshocked labradorite shows strong,
769 narrow peaks. Both fused glass and maskelynite exhibit only broad peaks near 496 and 1030 cm^{-1}
770 .

771 Figure 3: NNR spectra of maskelynite. A) ^{29}Si B) ^{27}Al, C) ^{23}Na. Data are presented in Table 1.
772 For ^{29}Si, ^{27}Al, and ^{23}Na, maskelynite is clearly less ordered than the crystalline labradorite. The
773 ^{29}Si peak is slightly narrower than fused glass. The opposite is true for ^{27}Al and ^{23}Na, where
774 maskelynite shows a slightly broader peak than fused glass.

775

776 Figure 4: Structure factor *S(Q)* of three different maskelynite samples (Mask_1 red line, Mask_2
777 blue line, Mask_3 green line) and a fused glass with anorthite composition. Even despite
778 compositional differences between maskelynite (An_{63}) and fused glass (An_{100}), the different
779 samples are undistinguishable on basis of the structure factor.

780 Figure 5: The pair distribution function *G(r)* of different maskelynite samples and fused glass.
781 The inset show the region characteristic for the intermediate range order in the atomic
782 arrangement.

783

784 Figure 6:

785 The pair distribution function *G(r)* of different orientations of maskelynite samples The inset
786 show the region characteristic for the intermediate range order in the atomic arrangement.

787

788

789 Figure 7 –Micro-FTIR spectra of rotated samples. For each, the sample was mounted in an epoxy
790 mount, and the entire block was rotated 90 degrees to obtain measurements of multiple
791 orientations through the sample. A) unshocked labradorite, B) fused glass of labradorite
792 composition, and C) maskelynite (of labradorite composition). Rotating unshocked labradorite
793 corresponds with shifts in peak positions from 1175 cm^{-1}, and 1001 cm^{-1}, to 1110 cm^{-1} and 920
794 cm^{-1} with a shoulder at 990 cm^{-1}. Fused glass has only one peak at 995 cm^{-1}, independent of
795 orientation. Maskelynite has one peak, but upon rotation the peak position changes from 1000
796 cm^{-1} to 960 cm^{-1}.

797

798 Figure 8: Backscatter electron images of 2 maskelynite grains. Compositional data shown in
799 table 2, with analysis locations indicated by yellow dots. Even though the maskelynite is
800 optically isotropic, strong oscillatory zoning (A) is preserved.

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