Changes in Mineralogy and Geochemistry of Quartz and Feldspars in Response to Impact Cratering

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Changes in Mineralogy and Geochemistry of Quartz and Feldspars in Response to Impact Cratering

A Dissertation Presented

by

Steven J. Jaret

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The Graduate School

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Impact cratering is an important geologic process that has affected all objects in the Solar System. The goal of this work is to understand how this process affects the mineralogy and geochemistry of planetary surfaces. Studies of extraterrestrial materials (e.g., laboratory studies of meteorites) and studies of planetary surfaces via orbiter or lander missions encounter impacted and shocked materials. Therefore, knowing how this secondary process of cratering has altered the rocks and minerals is critical to our ability to deconvolve the secondary effects of shock from the original primary geology. Specifically, I seek to understand impact metamorphism in three ways: 1) identification and characterization of impact materials using a variety of optical and spectroscopic techniques, 2) identification and characterization of the mineralogical structure changes and mechanisms associated with impact cratering and 3) constraining how structural changes affect geochemistry, particularly our ability to obtain radiometric dates of these samples.
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Chapter 1

1.1 Summary of Chapters

Chapter 2 is a detailed study of naturally shocked plagioclase from the Lonar Crater, India. Using a variety of spectroscopic techniques (micro-FTIR, micro-Raman, X-Ray total scattering, and Nuclear Magnetic Resonance), I show that naturally shocked plagioclase transforms to an amorphous material (“maskelynite”) without undergoing melting. This is important because the presence or absence of melt affects other geochemical processes. Therefore, determining whether or not melting has occurred directly impacts our geologic interpretations. For example, melt will produce new grains or crystals, whereas solid-state processes may not. This work was published in the Journal of Geophysical Research: Planets in 2015.

Chapter 3 focuses on the formation of the high-pressure, high-temperature SiO$_2$ phase coesite in the same naturally shocked samples from the basaltic Lonar Crater, India situated in the Deccan Traps. This is the first identification of coesite at the Lonar Crater. The coesite is unusual and is restricted to only within amygdules in the shocked basalts. I suggest that this coesite formed directly from molten SiO$_2$, due to extremely localized melting in response to collapsing vesicles during the impact. Similar spikes in temperature along cracks and fractures are common in meteorites, but have not previously been reported for terrestrial samples. This chapter also highlights the importance of heterogeneities during impact, allowing for local melting within a rock that did not undergo wholesale melting. This work was published in Meteoritics and Planetary Science in 2016.

Chapter 4 is an argon isotopic study of maskelynite from the Manicouagan impact structure, Canada. Building on the work of chapters 1 and 2, I first characterized these samples spectroscopically to show they underwent purely solid-state deformation. Then, I conducted $^{40}$Ar/$^{39}$Ar isotopic analyses to obtain ages of the maskelynite. This was compared to unshocked target rocks and impact melt from Manicouagan. Interestingly, the maskelynite does not yield the age associated with either the target rock or the impact melt. And furthermore, the age-release spectrum does not follow patterns similar to partial resetting in thermal metamorphic environments. The implication of this study is that argon isotopic analyses (which are commonly used on martian and lunar samples) are not reliable for dating shocked materials. This work has been submitted to Nature Geoscience and is currently under review.
Chapter 5 is a combined petrographic, and spectroscopic study of experimentally shocked plagioclase. The goal of this chapter is to characterize samples with micro-Raman and micro-FTIR spectroscopy in order to directly compare samples of known shock conditions to naturally shocked feldspar. Here I show that increasing shock level corresponds to changes in crystallinity. However, at the micro-scale, shock effects are heterogeneously distributed throughout the sample. This work highlights the importance of spatial scale and the critical differences between micro-analytical techniques and bulk or whole-rock analyses that average across multiple grains and crystal orientations. This work is currently being prepared for publication in the *Journal of Geophysical Research: Planets* and will be submitted this summer.

1.2 Background

1.2.1 Impact Crater formation

Impact craters result from the hypervelocity collision of an asteroidal or cometary body with the surface of a planetary object. Because a large object retains its Solar System velocities, its collision with a planetary surface produces a shock wave in both the target and the impactor. When the shock wave reaches the back of the projectile, it is reflected forward as a rarefaction wave (also called a release wave) which decompresses both the projectile and eventually the target. The impact itself occurs in three phases: i) contact and compression, ii) excavation, and iii) modification. Contact and compression is the initial dramatic increase in pressure (and temperature) due to the transfer of kinetic energy of the impactor into the target rocks via a shock wave until the end of the passage of the rarefaction wave. This phase has been studied primarily from a theoretical standpoint and through application of work from nuclear explosion tests (Gault et al., 1968; Kieffer and Simmonds, 1980; Melosh, 2013, 1989; O’Keefe and Ahrens, 1975; Roddy et al., 1977).

The excavation phase immediately follows contact and compression and is the stage of cratering where the physical crater is opened due to complex interactions between the ground surface and the expanding hemispherical shock wave (Dence et al., 1968; French, 1998; Grieve and Cintala, 1992; Melosh, 1989; Osinski and Pierazzo, 2013). Descriptions of the excavation stage are typically focused on the formation of the transient crater, which is the maximum cavity created by the flow of material outward from the impact, before entering back into a gravity controlled regime. During this stage, target rocks are shocked, fractured, melted, ejected, and
displaced significantly from their original locations. Additionally, shock metamorphic features (see below) are created during this stage of cratering.

Lastly, the modification stage is defined as all modification to the impact structure after the transient crater has reached its maximum size. Geologically, I prefer to think of this as multiple stages of modification. The first is impact-related modification. After the transient crater reaches its maximum diameter, gravitational forces take over producing inward flow of material back into the crater, collapse of the crater rim, settling, normal faulting of blocks both into and away from the crater, backthrusting and/or folding of the rim, and deposition of ejecta both into and outside of the crater (French, 1998; Melosh, 1989). Depending on the specific geology of the crater, this point can also initiate short-lived hydrothermal systems (Kirsimae and Osinski, 2013). All these things are associated with the impact itself, but because they occur after the passage of the shock wave they are considered part of the modification stage.

The second phase of modification consists geologic events that affect the impact structure, but significantly post-date the impact event. This includes erosion, burial, and overprinting by tectonics. Traditional texts on impact structures (French, 1998; Melosh, 1989; Osinski and Pierazzo, 2013) do not distinguish these as separate stages. However, particularly for studies of terrestrial impact structures where you currently observe the collective result of all geologic activity since the impact structure formed, it is important (and frequently difficult) to distinguish and recognize what is related to the impact event and what is not.

1.2.2 Impact Metamorphism

During compression and excavation target rocks undergo a progression of deformation collectively referred to as impact metamorphism. This includes brecciation, melting, formation of high-pressure, high-temperature polymorphs, internal mineral deformation and amorphization, and in some cases vaporization. Within this, a subset of deformation features, (referred to as “shock deformation”) have been specifically tied to the passage of the shock wave (e.g., formation of planar deformation features) and serve as unique indicators of an impact. While this distinction may seem subtle, shock metamorphism has a much more restricted set of formation conditions than the broader set of impact metamorphic features. Shock metamorphism follows shock physics along the hugoniot unlike sub-shock acoustic deformation in tectonic events. Importantly, this means that only shock metamorphic features can be considered uniquely diagnostic of impact
events. For example, brecciation and the formation of high-pressure, high-temperature polymorphs both occur in non-impact settings. For the purposes of terrestrial studies, particularly identification of new structures, it is useful to separate shock metamorphism from impact related features that are not unique to shock waves.

1.2.3 Shock Metamorphism and Petrography

Most of the early work on shock metamorphism has been focused on transformations within silicates, specifically quartz and feldspars (Ahrens et al., 1969; Chao, 1968; Huffman and Reimold, 1996; Stöffler, 1971; von Engelhardt and Stoffler, 1968). In quartz, shock metamorphism is most frequently exhibited as planar deformation features (PDFs), which are defined as thin, 1-2 µm, planar lamellae that occur at specific crystallographic orientations. PDFs occur as sets of closely spaced lamellae (5-10 µm spacing) and frequently occur in multiple orientations per grain (Ferrière and Osinski, 2013). At the transmission electron microscopy (TEM) scale, PDFs are dislocation and appear amorphous within each deformation plane. Grains that have been subjected to post-impact heating, these often form “decorated PDFs” which are planes lined by fluid inclusions. In some cases PDFs are associated with high-pressure, high-temperature polymorph stishovite (Hamers et al., 2016). At higher shock levels, quartz becomes fully amorphous, but retains its original grain morphology, referred to as diaplectic quartz glass. Diaplectic quartz glass forms at slightly higher shock pressures and is interpreted to have formed through solid-state processes alone. The connection between PDFs in quartz and diaplectic quartz glass remains somewhat unclear. Huffman and Reimold (1996) have suggested that PDFs are the precursor to diaplectization, and that diaplectic quartz is a higher-level deformation extension of PDFs. A similar progression has been applied to feldspars, although the majority of studies of shocked feldspars have focused on the amorphization pressures only. This is discussed in detail in chapters 2 and 5.

1.2.4 Shock Barometry

The progressive nature of shock metamorphism has been long recognized and generally follows this path with increasing shock: brecciation, feature features, basal PDFs, single sets of PDFs at low index, high-index PDFs, diaplectic glass, melting, and vesiculation (Chao, 1968; von Engelhardt and Stoffler, 1968). Based on the petrographic trend of shock textures, several
classification schemes for assessing shock level in natural samples have been suggested (Chao, 1968; Kieffer et al., 1976; Singleton et al., 2011; Stöffler, 1971; von Engelhardt and Stoffler, 1968).

Frequently, the goal of studies of shock metamorphism is to determine specific impact conditions based on shocked materials both on the earth and in meteorites. This is typically done using co-occurrence of mineral phases (e.g., high-pressure, high-temperature phases or formation of amorphous material eg. Stoffler 1971; von Engelhardt and Stoffler 1968; Horz and Quaide, 1972; Ostertag 1983; Huffman and Reimold 1993) and or by orientation measurements of shock textures. Shock experiments (Grieve and Robertson, 1976; Robertson and Grieve, 1977; Stöffler and Langenhorst, 1994) have shown that the orientation of PDF planes with respect to the c-axis in quartz is pressure dependent. This has led to shock barometry calibration studies (Holm et al., 2011; Robertson and Grieve, 1977) which attempt to assign impact pressures to shocked samples in natural craters. One of the challenges, however, is that assigning pressures based on petrography is difficult (Fritz et al., 2017) and has led to classification schemes that divide shock into broad categories with pressure uncertainties of ~15-30 GPa.

1.2.5 Shock Pressure Calibrations

For both quartz and feldspar there have been many attempts to associate formation pressures to transformations within feldspars in response to shock. Two methods have been used: i) static compression within diamond anvil cells and ii) shock experiments. Presently there remains a discrepancy in pressure estimates for important petrographic and structural changes determined by these two methods. This topic has been the subject of debate for nearly 40 years, particularly over how to interpret conditions in meteorite parent bodies with estimates differing by as much as 40 GPa (Fritz et al., 2017; Gillet and Goresy, 2013; Sharp and Decarli, 2006). I have summarized some of this below and elaborate in chapter 5.

1.2.6 Static Experiments

Static compression experiments operate on very small sample volumes (~100 µm grains) and consist of slow compression in diamond anvil cells. These experiments occur over long time scales (minutes to hours) and are typically stepped, where pressure is increased, paused to take measurements, then stepped up again until desired pressure is reached. Pressure is measured by X-
ray or Raman spectroscopy of calibration standards (typically ruby, e.g., Dewaele et al., 2008; Mao et al., 1986) within the cell. This assumes that the compression within the cell is hydrostatic and that the standard and the sample experience the same pressures. Unfortunately, perfectly hydrostatic compression is difficult to achieve at high pressure (above 20 GPa). One other potential discrepancy between static compression experiments and natural impacts is that in static experiments the sample is measured while under compression. In natural impacts, however, samples measured have been shocked to high pressure but are measured post-impact now under ambient pressure and temperature conditions.

1.2.7 Shock Experiments

Another method of studying shock effects is using shock experiments (for detailed reviews of experiments see Langenhorst and Hornemann, 2005; Sharp and Decarli, 2006). Commonly used are flat plate accelerator experiments in which metal plates are accelerated at ~1-3 km/s via onto flat samples (typically ~1cm by 0.5 cm discs) by heavy explosives. This produces a planar shock wave in the target. Pressures are measured by optical interferometry during the experiments and assume uniform pressures across the sample. To achieve high pressures, the reverberation technique is used. Because the sample is thin the shock wave reflects multiple times between the sample surface and the container. This has the advantage of being easier for sample recovery, and allowing for achieving high pressure using significantly lower accelerating velocities. Reverberation experiments, however, have important disadvantages. First, unlike natural impacts, these experiments take multiple shots to achieve max pressure. Secondly, reverberation experiments generate significantly lower temperatures than in natural impacts. Third, shock experiments have durations of <1 µs compared to ~1s in natural impacts. This causes drastically different strain rates, which may be critical for how minerals are internally deformed. Of course, no lab experiment can perfectly recreate a natural impact, so by combining what we learn from both static and shock experiments we may be able to get a better sense of what occurs in natural settings.

1.2.8 Geochemistry of Impacts

Geochemical studies of impact rocks generally have one of 3 objectives: i) identification and characterization of impactor components (Koeberl, 2002); trace element and isotopic studies
of impact melt products (e.g., O’Connell-Cooper and Spray, 2011; Shaw and Wasserburg, 1982); and iii) geochronology of impact events (e.g. Jourdan et al., 2009). I have focused primarily on the geochronology aspect (see chapter 4). Understanding the timing of impact events is crucial for our interpretations of events both on the Earth and on other planetary bodies. On the Earth, impacts have been implicated in major evolutionary events such as mass extinctions (e.g., (Alvarez et al., 1980; Bodiselitsch et al., 2004). In order to definitively demonstrate these events to be related, we must be able to both precisely and accurately determine the timing of impact events. For the Moon, lunar stratigraphy is based on superposition and deposition of ejecta layers, and therefore having precise and accurate ages of the impact events is critical and would allow for assessment of rates for early lunar events. For Mars, there is significant controversy over how we interpret surface ages because our limited sample set may have been overprinted by impact events. As I will show in chapter 4, dating impact events is complicated and understanding the full history of the samples is often required.

In summary, this dissertation consists of 4 individual projects that focus on the micro-structural and geochemical changes in response to natural and experimental impacts. The themes that remain critical to answering questions of impact processes here are the role of melting during impact and the role of small spatial-scale heterogeneities. Impacts are complex and require a detailed, multi-technique approach in order to completely capture all of the geological processes and changes that occur.

1.3 References
Impact Cratering: Processes and Products.


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Chapter 2

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

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2.0 Abstract

We present the results of a combined study of shocked labradorite from the Lonar Crater, India, using 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. 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 preservation of some intermediate range order – which are all consistent with a solid-state transformation from plagioclase to maskelynite.

2.1 Introduction

Across the Solar System, impact cratering has played a major role in modifying the surfaces of planetary bodies. On Earth, impact events are important for the evolution of the 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 major crustal recycling processes allows for greater preservation of the impact cratering record, yielding large expanses of heavily cratered terrain. This terrain is frequently the target of robotic missions because of the potential for exposure of deep crustal lithologies. The Opportunity Rover has already encountered material interpreted to be impact ejecta on Mars in Meridiani Planum (e.g. Bounce Rock, Zipfel et al., 2011). The minerals in such material, however, may have been affected by shock. In fact, many of the martian meteorites, particularly the shergottites, show evidence of moderate to high shock
Correctly interpreting the geologic histories of heavily cratered planetary bodies requires a full understanding of the crystallographic and structural changes of major minerals induced by shock. To address this issue, we investigated the structural differences between plagioclase and maskelynite of plagioclase composition because plagioclase is a major component of martian and lunar crustal rocks. In this paper, we first review nomenclature, previous analyses and interpretations regarding maskelynite. Then, we describe the structure of the maskelynite from the Lonar crater and compare it to that of crystalline plagioclase and fused plagioclase-composition glass. Lastly, we discuss possible formation mechanisms and conditions.

2.2 Background
2.2.1 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 largely obliterated through melting and/or vaporization and the target rocks undergo a progression of deformation effects (French and Short, 1968; Stöffler, 1971; Melosh, 1989; Osinski and Pierazzo, 2013 and references 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 Engelhardt and Stöffler, 1968; French and Koeberl, 2010; Osinski and Pierazzo, 2013, and references 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 Earth, the majority of studies of shock metamorphism have focused on the mineralogic changes in tectosilicates, specifically quartz and feldspar, which are known to have crystal structures more susceptible to shock deformation than other silicate types (Stöffler et al., 1991; Johnson et al., 2002; Langenhorst, 2002).

For extraterrestrial materials, shock effects in plagioclase are most relevant for studies of basaltic or anorthositic surfaces, which commonly occur on Mars and the Moon. Shock effects in plagioclase, while less commonly studied than shock effects in quartz, have been well documented

Unfortunately, shock classification and barometry calibration is complicated by multiple classification schemes (Short 1969; Chao, 1968; Stöffler, 1971; Kieffer et al, 1976; Singleton et al., 2011). In this paper, we follow the classification scheme of Kieffer et al. (1976) because it was developed using shocked Lonar basalts.

Regardless of the specific classification scheme used, feldspars generally behave similarly during shock. A major change in plagioclase crystal structure occurs at shock pressures of ~28-34 GPa, at which point plagioclase transforms to a diaplectic glass, often referred to as maskelynite (Bunch et al., 1967; Ostertag, 1983). Interestingly, the transition to maskelynite is gradational and highly variable depending on specific pre-shock rock properties (e.g., composition, grain size, porosity, etc) and in some cases plagioclase can retain partial crystallinity up to ~45 GPa (Ostertag, 1983). Specific feldspar composition directly affects the pressures at which the transition to maskelynite occurs, where more calcic feldspars transform at slightly lower pressure than the more sodic endmembers (Ostertag, 1983; Williams and Jeanloz, 1988, Johnson et al., 2002, 2003).

This loss of crystallinity in plagioclase marks a major transition resolvable optically and spectroscopically. Thus, the plagioclase-maskelynite transformation has been the focus of intense research for over 50 years (Milton and DeCarli, 1963; Bunch et al., 1967; Stöffler, 1971; Hörz and Quaide, 1973; Bischoff, and Stöffler, 1984; Ostertag, 1983; El Goresy et al., 1997; Chen and El Goresy, 2000; Fritz et al., 2005; El Goresy et al., 2013).

2.2.2. Maskelynite Formation

Despite multiple studies of maskelynite, there remains considerable debate over its formation mechanism. Much of the debate centers around whether or not it forms via solid-state deformation as a diaplectic glass (Bunch et al., 1967; von Engelhardt and Stöffler, 1968; Hörz and Quaide, 1973), after shear induced melting (Grady, 1980), or forms via quenching from a melt as
a fused glass under high pressure (Chen and El Goresy, 2000). Solid-state and melting-related formation mechanisms are distinct processes and have different implications for the geochemical behavior of the rock during impact deformation. Most importantly for understanding geochronology, melting and quenching of a fused glass would produce a new material whose age would reflect the time of impact. However, a solid-state mechanism for maskelynite formation need not necessarily reset isotope systems. Unfortunately, nomenclature is muddled in the literature with maskelynite and diaplectic glass often used interchangeably (Tschemark, 1872; Bunch et al., 1967; Stöffler, 1971; Arndt et al., 1982; Ashworth and Schneider, 1985; White, 1993; Chen and El Goresy, 2000) without clear knowledge of the specific formation mechanism.

Even within these two genetic models (melt vs. solid-state), the exact formation mechanism is unclear. Multiple hypotheses have been proposed for both static and dynamic compression of silicates. Solid-state models (aka diaplectic glass models) include: (1) reversion of high pressure phases to glass (Ahrens et al., 1969; Williams and Jeanloz, 1988); (2) metamict-like destruction of the order at the unit cell scale (Ashworth and Schneider, 1985); and (3) pressure-induced formation of high coordination glasses (Hemley et al., 1988).

Models involving melting include: (4) shear-band induced melting (Grady et al., 1977; Grady, 1980) and (5) quenching of dense melt under high pressure (Chen and El Goresy, 2000). Although these models have all been applied to plagioclase (White, 1993), many of the diaplectic 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 all framework silicates behave similarly. Only a few studies (Hörz and Quaide, 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 minerals for the purpose of better constraining the formation process. This paper presents an integrated approach using multiple techniques, applying them to the same sample in order to minimize the chance that the samples investigated with each structural tool have seen different extents of shock modification.

2.2.3 Optical Petrography
Maskelynite, initially identified in the martian basaltic meteorite Shergotty (Tscharmack, 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 between maskelynite and pyroxenes such that the texture of the target rock remains. However, the maskelynite has a lower refractive index than unshocked plagioclase. Additionally, in cross-polarized light, maskelynite is easily distinguished from unshocked plagioclase as it is optically isotropic (Figure 2.1).

2.2.4 Raman Spectroscopy

Raman spectroscopy, a vibrational spectroscopic technique based on inelastic scattering of monochromatic light, 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 (Velde and Boyer, 1985; Chen and El Goresy, 2000; Fritz et al., 2005; Jaret et al., 2014).

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

2.2.5 Nuclear magnetic resonance (NMR) spectroscopy

Solid-state nuclear magnetic resonance (NMR) spectroscopy observes nuclear spin transitions as a way of characterizing local chemical environment (Stebbins and Xue, 2014). This technique is particularly useful for analysis of amorphous material because it is sensitive only to
local environment and not long-range order. Specifically, for NMR, the peak position, or chemical shift, of $^{29}$Si in silicates is representative of the number and length of Si-O bonds, the types of next nearest neighbor atoms, and other structural features such as Si-O-T bond angles. The peak width reflects the distribution of chemical shifts, providing a measure of disorder, and the area under the peak is proportional to the number of nuclei in that local environment. In silicates, the $^{29}$Si chemical shift is most strongly affected by coordination number. Increasing the coordination number (i.e., increasing the mean cation-oxygen distance) generally corresponds to decreasing the chemical shift (Stebbins and Xue, 2014 and references within). Thus, NMR spectroscopy may be a particularly useful tool for studying shocked material since changes in cation-oxygen distances, increasing coordination number of cations, disordering of materials, and formation of glasses all can occur in response to impact events. NMR spectroscopy utilizing other nuclei, such as $^{27}$Al and $^{23}$Na in this case, can also provide information on structure in terms of cation-oxygen coordination number. However, peak widths and positions for these nuclei are also affected by nuclear quadrupole effects which complicates interpretation of peak width strictly in terms of disorder. For example, highly distorted sites in otherwise well-crystalline minerals also yield broad peaks, with a width related to the magnitude of quadrupolar coupling ($C_q$, product of the nuclear quadrupole moment and the largest component of the electric field gradient at the nucleus) and fine-structure determined by the departure of the electric field gradient from axial symmetry.

Nuclear magnetic resonance (NMR) spectroscopy of shocked minerals has largely been limited to SiO$_2$ (Fiske et al., 1998; Boslough et al., 1995; Lee et al., 2012, Yang et al., 1986). Few studies have investigated feldspar, and these have been primarily focused on the low-shock regime, at pressures below the transition to maskelynite (Cygan et al., 1992). They report that up to ~22 GPa shock pressures no systematic changes to Si or Al coordination can be detected. More recently Lee et al. (2012) used $^{27}$Al NMR spectroscopy to show that shock compression of a basalt-like diopside-anorthite composition glass produces higher coordinated Al environments.

2.2.6. X-ray Total Scattering

X-ray scattering can be used to determine crystal structure, yielding position of atoms in solids. In contrast to conventional X-ray powder diffraction, which relies solely on Bragg intensities and positions to determine average long-range order, X-ray total scattering experiments collect both Bragg and diffuse scattering and treat them equally. This provides a more direct and
precise measurement of interatomic distances and structural order and is particularly useful for amorphous materials which generally lack long-range atomic order (see Reeder and Michel, 2013 for full technique review). Fourier transforms of total scattering experiments yields a pair distribution function, which represents a distribution of interatomic distances weighted on the basis of scattering power of atom pairs. Pair distribution peaks between 1 and 3 Å are usually interpreted as bond length in the first coordination shell. Peaks between 3 and 4 Å represent distances in the 2nd and higher coordination shells. Peaks between 4 and 20 Å represent intermediate-range structure associated with connected polyhedral units.

To date, X-ray total scattering experiments have not been applied to shocked materials. Numerous conventional X-ray diffraction studies, however, have been conducted on shocked tectosilicates (Hanss et al., 1978; Arndt et al., 1982; Ostertag, 1983; Diemann and Arndt, 1984). These studies show that for both naturally and experimentally shocked samples the silicate structure collapses with impact pressure (Hörz and Quaide, 1973; Pickersgill et al., 2014). Both Debye-Scherrer (powders) and target micro-XRD measurements of individual grains show that increasing shock level corresponds to increased asterism and streaking along Debye rings (Hörz and Quaide, 1973; Pickersgill et al., 2014). This breakdown of the crystal lattice is progressive, and strongly correlates with shock pressure, and because of this, XRD has been suggested as a tool for analytically quantifying shock pressures (Hörz and Quaide, 1973; Pickersgill et al., 2014).

Diemann and Arndt, (1982) compared diaplectic glass from the Manicouagan impact structure to a fused glass (at atmospheric pressure) of similar composition. They concluded that there is little structural difference between the fused glass and diaplectic glass. However, they also state that in some cases the diaplectic glass may be slightly less disordered than fused glass. They interpret this to reflect “relics” of 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 either incomplete or heterogeneous transformation to diaplectic glass, which is commonly seen petrographically at Manicouagan (Thompson, 2014).

2.2.7. 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)O₄ tetrahedra (Iiishii et al., 1971). Bending vibrations in the Si-O-Al planar ring occur between 400 and 550 cm⁻¹. Octahedral stretching of SiO₆ 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 the strength of 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).

2.3. Samples and Methods

2.3.1. Samples

The samples used in this study were collected at the Lonar Crater in 2005, 2006, and winter Dec. 2009 – Feb. 2010 (S. Wright). The Lonar Crater, India, is a rare terrestrial impact site, as it is the only terrestrial impact (of ∼190 known) emplaced entirely into flood basalt target rocks (Son and Koeberl, 2007; Earth Impact Database, 2011, available at http://www.passc.net/EarthImpactDatabase/index.html). The target lithology is a series of basalt flows, ranging in thickness from 5 to 30 m. Only minor petrographic differences (specifically the number and size of phenocrysts) occur between flows. Mineralogically, these rocks are dominated by 50% labradorite (An₆₅), 31% augite, 7% pigeonite, and 8% sulfide and iron-titanium oxides, and 4% other minor phases (Kieffer et al., 1976; Wright et al., 2011). Texturally, these rocks contain labradorite phenocrysts up to 2 mm in diameter in a fine-grained groundmass (~0.2 mm). Shocked samples for this study consist of Class 2 basalt (“LC09-253,” see (Wright et al., 2011)), which was a clast in the suevite (impact melt-bearing breccia) in the proximal ejecta blanket (Kieffer et al., 1976; Wright et al., 2011; Wright and Newsom, 2013; Wright, 2014). For comparison to crystalline labradorite, we used samples from Ajanta (“AJ-101”), collected from
the Deccan flows, but away from the crater proper (Wright et al., 2011). For comparison with fused glass we prepared synthetic labradorite glass ($An_{60}$).

2.3.2. Methods

For comparison to maskelynite and unshocked labradorite, we synthesized fused glass of labradorite composition. We separated labradorite grains from unshocked Deccan basalts with a Selfrag electromagnetic separator to ensure a pure starting material. A total of 100 mg of separated labradorite grains were heated in a Deltec furnace to 1500°C in a sealed Pt crucible for 90 minutes before quenching in air.

We conducted optical petrography on polished thin sections. NMR spectroscopy and X-ray total scattering experiments were conducted on powders and on separated single grains of maskelynite. Micro-FTIR spectroscopy measurements were conducted on oriented single grains, and on polished thin sections. Individual grains were separated using a Selfrag electro-magnetic separator at the Lamont-Douherty Earth Observatory and then hand-picked under binocular microscopes.

For our electron microprobe analysis, 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 minimize loss of K and Na.

We collected micro-Raman spectra using a WiTec alpha300R confocal imaging system, system in the Vibrational Spectroscopy Laboratory at Stony Brook University. It is equipped with a 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 sec integration time. All measurements used standard thickness polished thin sections.

We acquired MAS/NMR spectra for ~10 mg of separated maskelynite grains, a sample of crystalline labradorite of similar composition, and fused glass prepared from crystalline labradorite as described above. All samples were contained in 3.2 mm (o.d.) ZrO$_2$ rotors. The $^{29}$Si spectra were obtained with a 400 MHz (9.4T) Varian Inova spectrometer operating at 79.4 MHz. We used
3 μs single-pulse excitation (π/2) and 2 sec relaxation delays, corresponding to complete relaxation. Spectra for both $^{27}$Al and $^{23}$Na were collected with a 500 MHz (11.7 T) Varian Infinityplus spectrometer operating at 130.3 (27Al) or 132.3 MHz ($^{23}$Na) at a spinning rate of 20 kHz. The spectra were acquired with 1 μs pulses and 0.2 sec relaxation delays, where the non-selective π pulse length was 10 μs (νRF = 50 kHz). We also acquired $^{27}$Al and $^{23}$Na multiple-quantum (MQMAS) spectra of selected samples at 9.4 T and 20 kHz spinning rate. The 3-pulse sequence employed excitation and conversion pulses of 2.2 and 0.8 μs for $^{27}$Al and 2.9 and 1.1 μs for $^{23}$Na (νRF = 120 kHz), and a 15 μs selective 90° zero-quantum filter pulse. The isotropic dimension was sampled with 20-36 points incremented by 25 μs (40 kHz spectral window in F1) using hypercomplex phase cycling for a total of 2400-9000 acquisitions.

High energy X-ray total scattering experiments used 10 mg of picked maskelynite grains, fused glass of labradorite composition as well as single 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) at wavelengths 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 parameters and the radial integration of the two-dimensional data (Hammersley et al., 1996). The total scattering function S(Q), which is the measured and normalized scattering intensity from the sample, was obtained using the program PDFgetX2 (Qiu et al., 2004) where standard corrections were applied as well as those unique to area-detector geometry (Chupas et al., 2003). The pair distribution function G(r) was generated by direct Fourier transformation of S(Q) with a Q$_{\text{max}}$ of 22 Å$^{-1}$.

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

2.4.1. Optical Petrography

In plane-polarized light, Lonar maskelynite occurs as phenocrysts and within the groundmass. Maskelynite appears uniformly smooth, lacking planar deformation features (PDFs), and planar fractures (PFs). Both phenocrysts and grains within the groundmass are euhedral to subhedral and show no textural evidence of melting (Figure 2.1A). In cross-polarized light, maskelynite grains remain at extinction through complete 360-degree rotation of the microscope stage (Figure 2.1B-E). No remnant or partial birefringence was observed. Pyroxenes, however, appear unaffected by shock, showing typical interference colors, and lack fracturing or granularization that is 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).

2.4.2. Micro-Raman Spectroscopy

As shown in Figure 2.2, unshocked labradorite exhibits characteristic peaks at 190, 482, 505, 561 Δcm\(^{-1}\) and lower intensity peaks at 270, 406, 778 Δcm\(^{-1}\) and a slight peak centered near 1030 Δcm\(^{-1}\). Fused labradorite glass exhibits two broad peaks at 495 and 1025 Δcm\(^{-1}\), with FWHM of 169 and 138 Δcm\(^{-1}\) respectively. There is also a slight shoulder at 559 Δcm\(^{-1}\). Maskelynite also exhibits two broad peaks at 482 and 1012 Δcm\(^{-1}\), with FWHM of 174 and 189 Δcm\(^{-1}\) respectively and a slight shoulder at 559 Δcm\(^{-1}\).

2.4.3 NMR Spectroscopy

NMR spectra and peak parameters for \(^{29}\)Si, \(^{27}\)Al, and \(^{23}\)Na are shown in Figure 2.3 and Table 1. The NMR spectra of Lonar maskelynite contain broad, featureless peaks that document an increase in the short-range disorder beyond the first coordination sphere. For example, the \(^{29}\)Si spectrum of maskelynite (Figure. 2.3A), shows a broad, approximately Gaussian-shaped peak for 4-coordinated Si centered near -91 ppm with a width of 18.6 ppm FWHM. We found no evidence
for 5- or 6-coordinated Si (chemical shift range ca. -150 to -220 ppm) in this spectrum nor in several others that were taken over extended periods and at both short and long relaxation delays (0.2 to 120 s) under conditions optimized to detect such species. In comparison, the spectrum of crystalline, un shocked labradorite is asymmetric and contains fine structure from resolution of distinct crystallographic sites and local environments with differing numbers of adjacent framework Al atoms. This spectrum is typical for those of intermediate composition plagioclase feldspars (Kirkpatrick et al., 1985), for which the signal is broad due to a wide range of chemical shifts for the different crystallographic sites and poorly resolved owing to short-range disorder in the occupancy of adjacent tetrahedral sites (i.e., Si-O-(Si,Al)). Surprisingly, the overall width and average chemical shift of the maskelynite peak is otherwise similar to those for the crystalline labradorite, indicating absence of large differences in the structure such as in the polymerization of the silicate tetrahedra. The average chemical shift is about 1.5 ppm higher for maskelynite, which can be interpreted as a small decrease in the average Si-O-T angle, of about 3° (e.g., Mauri, 2000). The slightly broader peak for maskelynite, by about 1 ppm, likewise can be interpreted as an increase in the range of Si-O-T bond angles. In contrast, the fused labradorite-composition glass yields a peak that is broader (3 ppm) than that for maskelynite with an average chemical shift that is shifted to slightly lower chemical shift compared to the crystalline labradorite.

Likewise, the $^{27}$Al and $^{23}$Na NMR spectra show evidence for peak broadening associated with disorder in maskelynite (Figure 2.3B-C), although these data are less easily related directly to structural differences. The $^{27}$Al NMR spectrum contains a broad asymmetric peak with a sharper edge at high chemical shifts and a broad tail extending to negative chemical shifts. This peak shape is characteristic of a range of quadrupolar coupling constants (Cq) arising from dispersion of electric field gradients at the nucleus (Coster et al., 1994; d’Espinose de Lacaillerie et al., 2008). The chemical shifts correspond approximately to the left edge of the spectrum, approximately 60 ppm, and are characteristic of 4-coordinated Al in a framework structure. The peak position is a complex function of the distribution of quadrupolar coupling constants and cannot be easily interpreted from these results. Although the broad tail overlaps the chemical shift range for 6-coordinated Al (near 0 ppm), the MQMAS spectrum (not shown) shows conclusively that nearly all of this signal intensity arises from tetrahedral Al having large peak width due to large Cq values. An additional, small feature occurs near +10 ppm, in the range for octahedral Al. The intensity of this shoulder varied among sub-samples suggesting that it could arise from an impurity, such as a
clay mineral. The MQMAS data also contain evidence for the presence of a small amount of 6-coordinated Al in the sample (<1%) but we could not ascertain with certainty whether this higher coordinated Al arises from the maskelynite or an impurity phase.

Comparison of the maskelynite $^{27}$Al NMR spectrum with those obtained for crystalline labradorite and labradorite-composition glass show a progression in the extent of the low-frequency tail and hence increase in the range of electric field gradients, from crystalline to fused glass to maskelynite (Figure 2.3B). Structurally, the electric field gradient relates to departure from cubic symmetry, which to first order can be associated with distortion of the Al coordination polyhedron from a perfect tetrahedron (although longer range factors also contribute). The Al tetrahedra in crystalline feldspars depart from tetrahedral symmetry, giving rise to the breadth and asymmetry of the peak for crystalline labradorite, but the extent of the local distortions is clearly much greater in maskelynite.

The MAS NMR results for $^{23}$Na (Figure 2.3C) are somewhat similar to those for $^{27}$Al in that the lineshapes are also affected by quadrupolar effects and show progressively larger width from crystalline labradorite to fused glass to maskelynite. The $^{23}$Na spectrum of maskelynite is more symmetrical than that for $^{27}$Al, as shown by the similarity of the peak position (-18.6 ppm) and average chemical shift (-20 ppm), suggesting that the peak width is less influenced by distribution of electric field gradients. The MQMAS data (not shown) indicate that much of the peak width can be attributed to a range of chemical shifts, which can be interpreted as dispersion in the weighted average Na-O bond distances (Angeli et al., 2000). Taken together the NMR spectra show that the structural disorder in maskelynite affects the local environment of both the framework cations and Na.

2.4.4 High Energy X-Ray Total Scattering

The structure factor S(Q) of the different maskelynite grains and the fused glass (An$_{60}$), and multiple maskelynite grains in a capillary are shown in Figure 2.4. 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 2.5. 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 a 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 provides insight into the connectivity of the local structure motif. Here, a significant difference of the intermediate range order can be observed between the maskelynite samples and the fused glass (inset Figure 2.5). The two maskelynite grains show a larger number of resolved maxima in the intermediate range in the G(r), compared with the G(r) of the fused glass. This indicates that in maskelynite, the intermediate range distances (4-10 Å) and dihedral angles have a narrower distribution, which represents an increased degree of atomic order. In comparison, the atomic arrangements in fused glasses can be described as continuous random network leading to a broad dihedral angle and distance distribution, which manifest as broader maxima in the pair distribution function G(r).

Figure 2.6 shows the G(r) of maskelynite grain 1 collected at a 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.

2.4.5 Micro-FTIR Spectroscopy

Unshocked labradorite from the Deccan region exhibits 2 primary peaks between 700 and 1300 cm\(^{-1}\), dependent upon orientation, as typical for labradorite (Rucks et al., 2015). 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 orientation 2, a small shoulder also develops near 990 cm\(^{-1}\) in addition to a peak near 900 cm\(^{-1}\), (Figure 2.7A). The fused glass of labradorite composition exhibits one peak centered at 995 cm\(^{-1}\), the position of which is independent of orientation (Figure 2.7B).

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$^{-1}$ (Figure 2.7C). All three grains measured showed similar behavior.

We investigated the magnitude of changes in micro-FTIR peak position as a function of composition by performing an electron microprobe analysis of the same individual grains measured with micro-FTIR. A comparison of peak position with An# is shown in Figure 2.8 and Table 2, where variations in peak position over the compositional range An$_{62}$ to An$_{69}$ are not well correlated. For example, the 8 grains of An$_{64}$ range in peak position from 987 cm$^{-1}$ to 1034 cm$^{-1}$. The 5 grains of An$_{65}$ range in peak position from 995 cm$^{-1}$ to 1030 cm$^{-1}$. Although we only have 2 measurements of grains with An# less than 62, we suggest a similar pattern would exist with a great sample size. Therefore, the implication is that these differences in peak position reflect the varying orientations of the grains in the rock more than any minor compositional variations in the samples.

2.5 Discussion

2.5.1 Comparison of maskelynite to fused glass and crystalline labradorite

Raman spectroscopy reveals that maskelynite is distinctly different from the crystalline labradorite, with a spectrum nearly identical to that of fused glass (Figure 2.2). There are slight differences between the maskelynite and the fused glass in both peak position and intensity. Fused glass shows a higher intensity of the 495 cm$^{-1}$ peak compared to the background. However, this is a minor effect and may simply reflect nonstructural sample differences, such as quality of the surface polish. The position of the fused glass and maskelynite peaks near 495 cm$^{-1}$ appear offset, but given the broad nature of these peaks, this difference in peak center may not be indicative of a compositional or structural difference. The pattern of two broad peaks centered near 495 cm$^{-1}$ and 1025 cm$^{-1}$ is also consistent with Raman patterns of synthetic fused glass of various plagioclase compositions (Sharma et al., 1983). It should be noted, however, we encountered one example of slight heterogeneity in the fused glass, suggesting there may have been minor areas that retained minor remnant crystallinity. As noted earlier by Treiman and Treado (1998), and confirmed here, Raman spectroscopy alone is insufficient for distinguish impact melt-glass (i.e., fused glass) from maskelynite despite common use for this purpose (Chen and El Goresy, 2000).
NMR results for $^{29}\text{Si}$ show that both fused glass and maskelynite yield just one symmetric peak, rather than an asymmetric partially resolved spectrum typical of crystalline labradorite (Figure 3), indicating absence of long-range order. The spectra of fused glass and maskelynite also differ; the peak for fused glass is 3 ppm broader than for maskelynite, and the average peak position is in the opposite direction from that for crystalline labradorite. These observations suggest that in terms of the range of Si-O-T bond angles maskelynite is more similar to crystalline labradorite than fused glass. In contrast, the broader $^{27}\text{Al}$ and $^{23}\text{Na}$ NMR signals from maskelynite indicate more distortion of the local coordination polyhedra. These differences between maskelynite and fused glass likely reflect differences in formation mechanism. Disordering by short-range atomic displacements would be expected to largely preserve the feldspar framework topology in terms of ring structure and range of Si-O-T angles, but could lock-in high-energy distortions of the coordination polyhedra, whereas quenched melt would contain a more random aluminosilicate network structure but lower-energy local bonding configurations. Both composition and quenching rate can affect peak width and position, but here the maskelynite and synthetic fused glass are compositionally similar (An$_{60}$ vs. An$_{63}$) and quenching of our synthetic fused glass was done very rapidly, ensuring high-energy local bonding configurations. We suggest that these differences between fused glass and maskelynite are reflecting differences in the style of structural disorder.

Recently, Lee et al. (2012) showed NMR evidence for shock-induced changes to Al coordination in experimentally-shocked fused glasses. They showed that after shock the $^{27}\text{Al}$ peak center moves towards a more negative chemical shift and the peak width increases and is associated with small amounts of higher coordination Al. Although our maskelynite does show some 6-coordinated Al, this might alternatively reflect a minor clay component, which is common in weathered plagioclase. This observation is consistent with the $^{29}\text{Si}$ NMR results discussed above.

The X-ray total scattering data show similarity on the length scale of the local structure between fused glass and maskelynite (Figure 2.4). Here, we compared maskelynite of An$_{63}$ composition to fused glass of labradorite (An$_{60}$) composition. Despite the minor compositional differences, there is no detectable difference in S(Q) between the fused glass and the maskelynite.

However, significant differences in the number and location of discrete maxima are observed in the intermediate range of the pair distribution function $G(r)$ between fused glass and
maskelynite. Maskelynite shows a higher degree of intermediate range order compared to fused glass (Figure 2.5-2.6).

Importantly, the residual anisotropy in the atomic arrangement of maskelynite observed in the G(r) of the same maskelynite grain in different orientations suggests that maskelynite is not formed through a melting process but rather through direct amorphization from a crystalline phase that preserves some of the framework topology. If maskelynite did form through a melting process, the G(r) obtained for maskelynite in two different orientations (Figure 2.6) would be identical, as it is expected for an isotropic solid such as fused glasses.

Although these maskelynite grains are optically isotropic at visible wavelengths, the orientation-dependent infrared reflectance peak position (Figure 2.7) suggests the maskelynite is not isotropic in the infrared. We replicated the IR experiments for 3 individual grains and the results shown in Figure 2.7 represent the measurements taken at as close to 90-degrees as possible. It should be noted, however, that the exact value of this peak position shift can vary depending on the specific crystallographic orientations are measured. For orientations that are less than 90 degrees apart, we measured differences in peak position of 40 and 60 cm$^{-1}$. Importantly, the exact value of difference in peak position is less diagnostic than the presence of shifting.

Similarly, we interpret the variation of peak position of maskelynite grains in thin section to also be due to orientation. Electron microprobe analysis of the same individual grains measured with micro-FTIR indicates no compositional dependence on peak position for these samples with limited compositional variation between An$_{62}$ to An$_{69}$ (Figure 2.8). For example, two grains of An$_{65}$ have micro-FTIR peak positions of 1026 and 995 cm$^{-1}$. Similarly, two maskelynite grains with micro-FTIR peak positions of 1018 cm$^{-1}$ have An#s of 57 and 64. Since we established there is no direct correlation between peak position and An# in these samples, it is therefore highly likely that the difference in peak position reflects the random orientations of the grains in the rock.

This interpretation is slightly different from previous work (Johnson, 2012), which concluded there are correlations between IR peak position and both composition and shock level. These data, however, may not be directly comparable, because of differences in range of compositional variability (differences between albite and bytownite compared to variation within labradorite) and because of differences in technique (emissivity measurements of chips and powders compared to IR reflectance of individual grains).
Previous infrared studies of maskelynite (Ostertag, 1983; Johnson et al., 2003) concluded that the spectrum of maskelynite was indistinguishable from the spectrum of fused glass. These studies differ from ours in that they measured powders and rock chips of larger samples, which included multiple grains at random orientations, rather than individual grains, resulting in an averaged orientation reflected in the spectra. By measuring multiple orientations of single grains, we show that that maskelynite is amorphous yet not necessarily isotropic at all wavelengths in the infrared.

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 infrared. Perhaps the IR detector is simply more sensitive and is able to detect changes that are not resolvable with our eyes.

Alternatively, and more likely, 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 with orientation decreases in such a way that at visible wavelengths there is no difference but at IR wavelengths, which start out with a large refractive index, there still remains 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 distances directly.

Our X-ray results are different from previous X-Ray studies that used powders (Ostertag, 1983), or unoriented micro-XRD (Pickersgill et al., 2014). Neither of the previously used techniques would be capable of detecting anisotropy because powders average orientation effects and analyses of a single orientation in thin section are not sufficient to detect anisotropy.

Importantly, the maskelynite grains in this study also show the preservation of original pre-shock igneous crystallization textures, as illustrated by the presence of oscillatory compositional zoning (Figure 2.9). The preservation of feldspar stoichiometry (Table 2.2) 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.

Zoning in terrestrial maskelynite has only been briefly noted from Lonar (Fredriksson et
al., 1979). Martian maskelynite, on the other hand, has received considerably more discussion.
Zoning from $\text{An}_{54}\text{Ab}_{44}\text{Or}_{2}$ to $\text{An}_{42}\text{Ab}_{54}\text{Or}_{4}$ has been reported in Shergotty and nearly identical
$\text{An}_{55}\text{Ab}_{43}\text{Or}_{2}$ to $\text{An}_{43}\text{Ab}_{53}\text{Or}_{4}$ is seen in Zagami, and maskelynite from EETA 79001 shows
oscillatory zoning (Treiman and Treado, 1998; Milkouchi et al., 1999). Such preservation of
zoning has been used to argue that this meteoritic maskelynite formed via solid-state processes.
Similarly, we find it difficult to envision a scenario where melting would preserve this texture
because of likelihood of cations, especially Na, diffusing during melting and subsequent cooling.

The use of zoning in maskelynite as an indicator of solid-state deformation has been
challenged by Chen and El Goresy (2000), who claim that zoning in Shergotty maskelynite is
restricted to partially birefringent grains and those with Raman patterns indicative of crystalline
(or partially crystalline) material. They therefore argue that the zoning in Shergotty maskelynite
reflects a region of the sample that has not experienced as high shock pressures. However, this is
not the case for our samples, as the same sample that exhibits preserved zoning has a Raman pattern
consistent with an amorphous material (Figure 2.2).

Our results highlight the importance of a multi-technique approach. Any technique –
particularly either Raman or unoriented infrared or X-ray techniques – may be insufficient to
properly distinguish crystalline plagioclase, maskelynite and fused plagioclase-composition glass.
Our analyses suggest that shock-produced maskelynite “glass” is fundamentally different from
fused glass because fused glass does not show any effect of orientation. For maskelynite, we
suggest these grains formed by short-range atomic displacements rather than melting without
internal homogenization resulting from long-range or diffusive movement of atoms within the
grain. Such a formation mechanism is consistent with the observed preservation of grain
boundaries and zoning of the maskelynite and lack of flow textures, suggesting a formation
mechanism purely via solid-state transformation (Stöffler, 1971; Hörz and Quaide, 1973) not
through quenching of a higher pressure melted glass (Chen and El Goresy, 2000; El Goresy et al.,
2013).
2.5.2 Formation mechanisms and conditions

Three specific models of solid-state formation of pressure-induced diaplectic glasses of silicate composition have been proposed: (1) reversion of high pressure phases to glass (Ahrens et al., 1969); (2) metamict-like disordering of the structure at the unit cell scale by short-range atomic displacements (Ashworth and Schneider, 1985); and (3) pressure-induced formation of high coordination glasses (Bunch et al., 1967; Hemley et al., 1988). Our results are consistent with any of these models. Even though we do not currently see Si or a significant fraction of Al with high coordination in these 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-to-diaplectic silica transformation, the shock wave deforms the crystal lattice in a similar way 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 to diaplectic plagioclase-composition glass transformation. Furthermore, annealing of metamict silicates leads to recrystallization and recovery of original structure (Tomasic et al., 1987; Bierrau, 2012), a property that also occurs in shocked diaplectic plagioclase-composition glasses (Bunch et al., 1967; Ostertag, 1983).

It has been well established that shock effects in plagioclase are progressive (Stöffler, 1971; White, 1993; Fritz et al., 2005; Jaret et al., 2014). 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. The Lonar maskelynite studied here exhibits only whole-grain type maskelynite. Based on petrography, this sample is a Class 2 basalt (Kieffer et al., 1976) with estimated shock pressures of ~25 – ~28 GPa. Although the maskelynite is fully optically isotropic at visible wavelengths, the pyroxenes remain birefringent (Figure 2.1), suggesting that the overall shock level was moderate in this sample. It is highly likely that the preservation of anisotropy within maskelynite occurs at moderate shock pressures just above the plagioclase-maskelynite transition. Therefore, our conclusions are only valid for
maskelynite of moderate-level shock classes. For maskelynite of the moderate-level shock classes, we favor solid-state mechanisms for its formation but other mechanisms such as the shear band model (Grady, 1977) may be applicable to other varieties of shocked feldspar such as higher shocked samples from Lonar or the PDF-type maskelynite of White, 1993.

2.6 Conclusions

We show that maskelynite formed at moderate shock level is the product of solid-state transformation and did not form through melting or quenching. Although maskelynite is isotropic at visible wavelengths and has Raman spectra identical to fused glass, X-ray total scattering data show a higher degree of intermediate range order and anisotropy in maskelynite. Additionally, infrared spectroscopy and X-ray total scattering experiments show differences due to orientation. Similarly, preservation of stoichiometric zoning within the maskelynite suggests minimal, if any, effect of heat during transformation to maskelynite. We favor a maskelynite formation mechanism that is purely solid-state, such as the mechanical disaggregation of the crystal lattice (Hörz and Quaide, 1973; Arndt et al., 1982) most likely by metamict-like destruction at the unit cell scale (Ashworth and Schnieder, 1985).

This study also presents the first spectroscopic technique to distinguish shock-produced glass from thermally produced glass, which not only has implications for the formation mechanism of 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 experiments onboard the Mars Curiosity Rover have 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. However, these techniques may be useful for distinguishing between shock-produced solid-state glass and fused glass in either martian meteorites or samples that are cached and eventually returned to Earth.

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Figure 2.1: Shocked basalt in thin section under

A) plane polarized light, showing the maskelynite (labeled M) and pyroxenes (labeled pyx).

B-E) cross-polarized light of the same location of the thin section as A, taken at 90-degree rotations of the microscopy stage. Specific stage orientations shown in the inset. This sample is thus a low-to-moderately shocked sample (Class 2) according to the shock classification scheme of Kieffer et al. (1976). Importantly, maskelynite is fully isotropic but no changes are seen in pyroxenes.
Figure 2.2: Micro-Raman spectra of unshocked labradorite (upper line, blue), fused glass (middle line, red), and maskelynite (lower line, green). Only the unshocked labradorite shows strong, narrow peaks. Both fused glass and maskelynite exhibit only broad peaks near 496 and 1030 $\Delta$cm$^{-1}$. The fused glass sample is significantly noisier than crystalline labradorite due to low raman scattering cross-section of glasses.
Figure 2.3: Comparison of A) \(^{29}\text{Si}\), B) \(^{27}\text{Al}\), and C) \(^{23}\text{Na}\) NMR spectra of maskelynite (bottom), An\(_{63}\) composition fused glass (middle), and crystalline labradorite. Corresponding spectral lineshape parameters are presented in Table 1. For \(^{29}\text{Si}\), \(^{27}\text{Al}\), and \(^{23}\text{Na}\), maskelynite is clearly less ordered than the crystalline labradorite. The \(^{29}\text{Si}\) peak is slightly narrower than that for fused glass. The opposite is true for \(^{27}\text{Al}\) and \(^{23}\text{Na}\), where maskelynite shows a slightly broader peak than fused glass. Asterisks denote positions of spinning sideband artifacts. Spectra are plotted as relative frequency shifts (parts per million, ppm) from standard reference materials tetramethylsilane (TMS; \(^{29}\text{Si}\)), and 0.1 m solutions of AlCl\(_3\) (\(^{27}\text{Al}\)) and NaCl (\(^{23}\text{Na}\))
Figure 2.4: Structure factor $S(Q)$ of four different maskelynite samples - 2 single maskelynite grains, assorted maskelynite grains in a capillary, and a fused glass with $\text{An}_{60}$ composition. Even despite compositional differences between maskelynite ($\text{An}_{63}$) and the fused glass ($\text{An}_{60}$), the different samples are undistinguishable on basis of the structure factor.
Figure 2.5: The pair distribution function $G(r)$ of 2 different maskelynite grains and fused glass. The inset show the region characteristic for the intermediate range order in the atomic arrangement.
Figure 2.6:
The pair distribution function $G(r)$ of 2 different orientations of a single maskelynite grain. The inset shows the region characteristic for the intermediate range order in the atomic arrangement.
Figure 2.7: Micro-FTIR spectra of rotated samples. For each analysis, the sample was mounted in an epoxy mount, and the entire block was rotated 90 degrees to obtain measurements of multiple orientations through the sample. A) unshocked labradorite, B) fused glass of labradorite composition, and C) maskelynite (of labradorite composition). Rotating unshocked labradorite corresponds with shifts in peak positions from 1175 cm\(^{-1}\), and 1001 cm\(^{-1}\), to 1110 cm\(^{-1}\) and 920 cm\(^{-1}\) with a shoulder at 990 cm\(^{-1}\). Fused glass has only one peak at 995 cm\(^{-1}\), independent of orientation. Maskelynite has one peak, but upon rotation the peak position changes from 1000 cm\(^{-1}\) to 960 cm\(^{-1}\).
Figure 2.8: Composition (plotted as An #) of maskelynite compared to micro-FTIR peak position of grains measured in thin section. Each point represents a different grain in thin section. All grains are fully isotropic at visible wavelengths. The shifts in peak position does not correspond to changes in An#, but are consistent with shifts due to orientation as shown in Figure 2.7C. Although we do not know the orientation of these grains in the thin section, we attribute the difference in peak position of different grains to reflect a preservation of intermediate order in the maskelynite.
Figure 2.9: Backscattered electron images of 2 maskelynite grains. Compositional data shown in Table 2.3, with analysis locations indicated by yellow dots. Even though the maskelynite is optically isotropic, strong oscillatory zoning (A) is preserved.
Table 2.1: Peak position, weighted average chemical shift (M1) and width (full width at half-height; FWHM) of NMR spectra obtained for crystalline plagioclase, fused An\textsubscript{60} composition glass, and maskelynite. All values in ppm. Data for Al and Na are values observed at 11.7 T, uncorrected for quadrupolar broadening and shifts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(^{29}\text{Si}) peak</th>
<th>M1</th>
<th>FWHM</th>
<th>(^{27}\text{Al}) peak</th>
<th>M1</th>
<th>FWHM</th>
<th>(^{23}\text{Na}) peak</th>
<th>M1</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>plag</td>
<td>-89.5\textsuperscript{1}</td>
<td>-92.7</td>
<td>17.6</td>
<td>56.0\textsuperscript{1}</td>
<td>50.8</td>
<td>18.9</td>
<td>-14.9</td>
<td>-16.4</td>
<td>12.8</td>
</tr>
<tr>
<td>An60</td>
<td>93.0</td>
<td>93.0</td>
<td>20.0</td>
<td>53.3</td>
<td>44.9</td>
<td>31.2</td>
<td>-19.7</td>
<td>-21.4</td>
<td>24.3</td>
</tr>
<tr>
<td>maskelynite</td>
<td>-91.1</td>
<td>-91.1</td>
<td>18.6</td>
<td>52.7</td>
<td>37.8</td>
<td>36.5</td>
<td>-18.6</td>
<td>-20.0</td>
<td>25.0</td>
</tr>
</tbody>
</table>

\textsuperscript{1} position of most prominent peak, several peaks present in the fine-structure.
Table 2: Chemical composition of maskelynite grains shown in Figure 2.9. Even though it is optically isotropic at visible wavelengths and has an amorphous micro-Raman pattern, pre-shock oscillatory zoning is preserved.
Chapter 3
An Unusual Occurrence of Coesite at the Lonar Crater, India
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3.0 Abstract
Coesite has been identified within ejected blocks of shocked basalt at Lonar crater, India. This is the first report of coesite from the Lonar crater. Coesite occurs within SiO$_2$ glass as distinct ~30 µm spherical aggregates of “granular coesite” identifiable both with optical petrography and with micro-Raman spectroscopy. The coesite+glass occurs only within former silica amygdules, which is also the first report of high-pressure polymorphs forming from a shocked secondary mineral. Detailed petrography and NMR spectroscopy suggest that the coesite crystallized directly from a localized SiO$_2$ melt as the result of complex interactions between the shock wave and these vesicle fillings.

3.1 Introduction
3.1.1 High Pressure SiO$_2$ Phases
Silica (SiO$_2$) polymorphs are some of the simplest minerals in terms of elemental chemistry, yet they are structurally complex with over 30 stable or metastable phases (Heaney et al., 1994). Two important polymorphs found in impactites are the high-pressure, high-temperature polymorphs coesite and stishovite. The first of these, coesite, is thermodynamically stable above 500°C and 2.5 GPa (Fei and Bertka, 1999; Liu and Bassett, 1986; Zhang et al., 1996). Crystallographically, coesite has monoclinic symmetry, but typically forms pseudo-hexagonal flakes when produced experimentally (Coes 1953; Ramsdell, 1955). Coesite can be distinguished from quartz optically as it has a refractive index of 1.59 – 1.604 and a density of 3.0 g/cm$^3$, compared to values of 1.54-1.55 and 2.65 for quartz.

The second high-pressure silica polymorph, stishovite (Stishov and Papova, 1961; Chao et al., 1962; Stöffler, 1971) forms at higher pressure-temperature conditions than coesite. Natural stishovite has only been reported from meteorites and terrestrial impactites (Ferrière and Osinski,
2013), where it is thought to form as a direct response to shock loading (Stöffler, 1971). Although there is no direct observation of non-shock stishovite in nature, a possible post-stishovite phase may be a large component of subducting slabs and the core-mantle boundary (Lakshtanov et al., 2007), and stishovite likely occurs in the deep mantle if basaltic slabs survive to depth. Additionally, two SiO\textsubscript{2} phases denser than stishovite have been identified in martian shergottites (El Goresy et al., 2001b, 2008).

Coesite was first produced experimentally (Coes, 1953; Ramsdall, 1955) and was subsequently identified in natural materials from the Meteor Crater, Arizona (Chao et al., 1960). Since then, coesite has been widely known as a shock feature related to impact events, although it also occurs in non-impact rocks such as kimberlites (Smyth and Hatton, 1977), and as inclusions within ultra-high-pressure eclogites (Chopin, 1984; Smith, 1984). Because of these non-impact occurrences, coesite can only be diagnostic of impact events if found in shallow crustal or surficial rocks and/or in a geologic context that sufficiently rules out high-pressure metamorphic conditions (French and Koeberl, 2010).

Despite often being described as an impact product, coesite has not been widely reported at terrestrial impact sites, having been identified at only 30 of the 186 (17%) known craters to date. (Figure 3.1 and Table 3.1). Furthermore, descriptions and interpretations of formation conditions regarding impact-produced coesite are commonly lacking. Of the 30 reports of coesite at impact structures, only 8 (4%) of those provide detailed petrographic context of the coesite (Table 3.1).

### 3.1.2 Coesite Formation Conditions

Many details of the quartz-coesite transformation remain unclear. Particularly in the impact setting, two remaining questions are i) the role of melting and ii) whether or not coesite can crystallize out of a melt or if it forms as a solid-state transformation. In impact settings coesite is most commonly interpreted to have formed via solid-state phase transformations that are associated with diaplectic quartz (Stöffler, 1971; Kieffer et al., 1976; Stahle et al., 2008; Ferriere and Osinski, 2013).

In some instances, impact-generated coesite is interpreted to have formed at high pressure after stishovite or a stishovite-like metastable phase (Stoffler, 1971; Kleeman and Ahrens, 1973). This hypothesis is based on observations made on samples taken at Ries crater, Germany, where stishovite and coesite co-occur but the coesite cuts across lamellar structures, which contain
stishovite. In this instance, coesite is thought to form behind the shock front, via pressure release from a stishovite-like phase (Dachille et al., 1963), or after pressure release from a silica phase of short-range order with four-fold coordination of Si (Stöffler, 1971).

Formation on pressure release may not be the only way coesite can develop. For example, coesite in terrestrial ultra-high-pressure samples (i.e., eclogites) is thought to form on compression, as supported by in-situ analyses of experiments at high pressure, which capture the quartz-coesite transition before the sample is released from high pressure (Perrillat et al., 2003). When coesite forms on compression, the higher-pressure phase stishovite is not required. Additionally, the quartz-coesite transformation conditions can vary depending on porosity and water content of the rock. In non-porous rocks, coesite formation requires pressures of 12-45 GPa, whereas porous rocks may only require 7-8 GPa (Osinski, 2007). It is worth noting however, that comparisons between static (e.g., eclogites) and dynamic (impact) coesite formation may be complicated because of sluggish kinetics of the reconstructive transition.

Because of the common association of impact-produced coesite with diaplectic quartz, the formation of coesite in this setting may require slightly longer shock pulses. Formation of coesite in association with diaplectic quartz may be restricted to >30 GPa, which is over 10 times greater than the pressure required in static equilibrium coesite synthesis (Stöffler, 1971; De Carli and Milton, 1965).

Furthermore, it remains uncertain if coesite forms only by solid-state processes or if it can also form as a direct crystallization product of silica-rich melts at high pressure. Synthetic coesite has only been produced in the lab via solid-state experiments, and impact-produced coesite is most commonly interpreted as a solid-state transition. However, Chen et al., (2010), suggested that the granular coesite at the Xiuyang crater, China, crystallized from a melt. Similarly, in a review of coesite at the Ries crater, Stahle et al., 2008 interprets two petrographic types of coesite, one of which may have formed from a melt, the other likely formed in though solid-state processes with either planar deformation feature (PDF) formation or diaplectic quartz.

3.1.3 Identification of Coesite

Coesite can be identified optically in thin section, and non-optically through analysis of bulk samples by techniques such as X-ray diffraction, Raman spectroscopy, infrared spectroscopy or nuclear magnetic resonance (NMR) spectroscopy. Optically, coesite is most commonly
distinguished by a high refractive index (1.594) and its two morphologies: fine grained needle-like crystals (Stöffler, 1971; Kieffer, 1971) or as greenish aggregates (a.k.a. “granular coesite”) (Stähle et al., 2008, Chen et al., 2010). The structure of coesite is monoclinic, and the crystal system has been well defined by X-ray diffraction analysis (Levien and Prewitt, 1981; Smyth et al., 1987).

3.1.4 Raman Spectroscopy

Raman spectroscopy is a technique that utilizes inelastic scattering of monochromatic light to probe the vibrational modes of materials, including low-frequency crystal lattice modes. As such, this is a useful tool for distinguishing among crystal structures, especially for material of identical chemical composition such as SiO$_2$ polymorphs and glasses. Raman (and micro-Raman) spectroscopy has been used for identification of coesite in both ultra-metamorphic and impact rocks (Boyer et al., 1985; El Goresy et al., 2001a; Ostroumov et al., 2002; Morrow, 2007; Liu et al., 2008). Coesite exhibits a strong peak at 521 Δcm$^{-1}$, which is attributed to symmetric Si-O-Si stretching mode. Additional vibrational modes include strong bands at 269 and 176 Δcm$^{-1}$ and slightly weaker bands at 425 and 355 Δcm$^{-1}$ (Sharma et al., 1981; Boyer et al., 1985; Ostroumov et al., 2002).

3.1.5 Nuclear Magnetic Resonance Spectroscopy

Solid-state nuclear magnetic resonance (NMR) spectroscopy is a technique that senses nuclear spin transitions as a way of characterizing the local chemical environment (Stebbins and Xue, 2014). This technique is particularly useful for analysis of amorphous material because it is sensitive only to local environment and not long-range order. Specifically for NMR, the peak position, or chemical shift, of $^{29}$Si in silicates is representative of the number and length of Si–O bonds, the types of next-nearest neighbor atoms, and other structural features such as Si–O–T bonding angles. The peak width reflects the distribution of chemical shifts, providing a measure of disorder, and the area under the peak is proportional to the number of nuclei in that local environment provided the spectra are acquired under conditions that avoid differential relaxation effects. In silicates, the $^{29}$Si chemical shift is most strongly affected by coordination number. Increasing the coordination number (i.e., increasing the mean cation-oxygen distance) generally corresponds to decreasing the chemical shift (Stebbins and Xue, 2014, and references therein).
Although not a routine analytical technique for impactites, NMR spectroscopy has been used previously for a few investigations of shocked quartz, coesite, and impact produced glasses (Fiske et al., 1998; Boslough et al., 1993, 1995; Lee et al., 2012, Yang et al., 1986; Cygan et al., 1990, 1993; Myers et al., 1998)

3.1.6 Lonar Crater, India
Lonar crater, India is a 1.8 km diameter crater located in Buldana district, Maharashtra state, India (Fredriksson et al, 1973), situated within the Deccan basalt flows. This crater has been well studied (Kieffer et al; 1976; Wright et al., 2011) and is of particular interest to planetary geologists because it is the only easily accessible impact structure into only basaltic rocks, making it an attractive lunar and martian analog (Maloof et al., 2010; Wright et al., 2011). Additionally, the composition of the Deccan basalts is similar to the surface type I spectral unit on Mars (Bandfield et al., 2000; Wright et al., 2011). The impact event is geologically recent, 570 ka (Jourdan et al., 2011), significantly younger than the 65 Ma target basalts. Importantly, during the time between the formation of the basalts and the impact event, there was significant aqueous alteration to the basalts, filling many of the basalt vesicles with zeolite, chalcedony, opal, and quartz. While these amygdules are likely hydrothermal in origin, their relationship to magmatic activity would require precise geochronology, which would be a challenge for these silica phases.

Here, we show that these secondary silica-rich phases were also shocked during the impact, producing coesite in a somewhat unusual location – only within amygdules in the vesicular basalts.

3.2 Samples
Shocked basalt, from maskelynite-bearing Class 2 through complete impact melts (aka Class 5), exists as clasts in a ~1 meter suevite breccia (aka impact melt-bearing breccia) (Kieffer et al., 1976). This unit overlies a thicker lithic breccia unit at Lonar crater (Kieffer et al., 1976; Wright et al., 2011). The three Class 2 shocked basalts (Kieffer et al., 1976) used in this study were collected in early 2010 by S.P. Wright from a suevite outcrop in the southern ejecta blanket, and were not talus. Similar to other Class 2 shocked basalts with aqueously-altered protoliths in Wright’s sample collection, the three Class 2 shocked basalts examined here contain decompression cracks suggested to be due to a change in volume during compression and decompression while remaining in the solid state throughout (Wright, 2013).
3.3 Methods

3.3.1 Optical Petrography

We employed optical petrography techniques with standard-thickness, doubly polished thin sections using an Olympus BH2 petrographic microscope using 20X and 40X objectives. In a few instances, we also used some slightly thicker sections (~60 microns) when there was a concern about losing material during thin-section making. Additionally, petrography was supplemented by secondary and backscattered electron imaging using a Focused Ion Beam (FIB) system, FEI Quanta 3D FEG Dual Beam at NASA’s Johnson Space Center.

The Focused Ion Beam (FIB) cross section/slice was prepared out of the coesite+glass region using the FIB (model: FEI Quanta 3D-FEG Dual Beam, using a Ga⁺ Ion Beam) to deposit Pt and to mill/sputter away material. The Region of Interest (ROI) was precisely selected and a Pt protective cap (35um L x 2.5um W x 2um thick) was deposited to preserve the ROI during FIB milling. After milling the front and back trenches the cross section was thinned down to ~0.5 um and both of the faces of slice were polished using low ion beam currents in the FIB. The cross section was then undercut (U-shaped) to isolate from the bulk and when completely cut, the thin section fell inside the cavity (formed by front and back trenches). The sample was taken out from the FIB chamber and transferred to the ex situ lift-out station where a thin tip glass needle was micro manipulated to fish out the FIB prepared slice, translated and placed on a sample stub.

3.3.2 Micro-Raman Spectroscopy

We collected micro-Raman spectra of polished thin sections in the Vibrational Spectroscopy Laboratory at Stony Brook University. For our measurements, we used a WiTec alpha300R confocal imaging system equipped with 532 nm Nd YAG laser with 50 mW nominal power at the sample surface and a 50X (0.80NA) objective with a spot size of 763 nm. Raman images were acquired over a 175 x 175 µm area with acquisition times of 0.1 sec. Single spectra were acquired with integration times of 60 secs for coesite and 240 secs for the glass.

3.3.3 Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy (MAS/NMR)

Silica vesicle fillings were separated from the host basalt using the Selective Fragmentation (SelFrag) electromagnetic separation instrument at Columbia University’s Lamont-Doherty Earth Observatory. The separated several filling of individual vugs was crushed and ~1.5 mg of powder loaded into a 3.2 mm (OD) ZrO₂ rotor. The ²⁹Si MAS/NMR spectra were obtained with a 400 MHz
(9.4 T) Varian Inova spectrometer operating at 79.4 MHz and a spinning rate of 12 kHz. We used 4 µs single-pulse excitation (π/2) and relaxation delays ranging from 2 to 1000 s for a total of 142,000 (2 s) to 414 (1000 s) acquisitions. For some experiments, the carrier frequency and short relaxation delays (Yang et al., 1986; Myers et al., 1998) were optimized for detection of signal from stishovite, but none was observed. Clear evidence for differential relaxation was observed in the spectra, but the limited amount of sample precluded extending the relaxation delays significantly beyond 1000 s, which required nearly five days of acquisition time. An attempt to obtain $^{27}$Al MAS/NMR data was conducted at 130.3 MHz (11.7T) and a spinning rate of 15 kHz using 1µs pulses (4.5 µs non-selective pi/2) and a 2 s relaxation delay. No stishovite signal was detected.

3.4 Results

Coesite was identified in three shocked basalt samples (LC09-253, LC09-294, and LC09-256). These samples are all of shock class 2 following the classification of Kieffer et al. (1976). In these samples, plagioclase has been completely converted into solid-state maskelynite but pyroxenes retain their birefringence (as previously described by Jaret et al., 2015; Wright et al., 2011).

3.4.1 Hand-Sample Petrography

In hand sample, the area of interest occurs within white amygdules (Figure 3.2A). On polished slabs, two phases are recognizable based on slight differences in hue. In some instances, amygdules exhibit a milky rind in addition to bright white centers.

3.4.2 Thin Section Petrography

In thin section, these two phases can be identified as silica glass and coesite. The silica glass is isotropic in cross-polarized light and in plane-polarized light lacks flow textures. Texturally, the coesite aggregates have two general morphologies: i) isolated individual aggregates embedded within the glass (Figure 3.2D-F), and ii) a closely packed network of aggregates (Figure 3.2B-C). This coesite network commonly forms on the edges of the vesicle, but occasionally occurs in the center of an amygdule (Fig 2B, D). Coesite occurs as 30-40 µm high-relief, greenish-
brown spherical aggregates of smaller crystallites (Figure 3.2E, F). In some instances, coesite aggregates appear to be nucleating around smaller crystallites. Additionally, some granular coesite aggregates have opaque grains (identified below as amorphous carbon) in the center of the sphere (Figure 3.2E).

3.4.3 Raman Spectroscopy

Micro-Raman spectroscopy was used to identify two phases within the silica vugs: crystalline coesite, a SiO$_2$ glass, and a rare amorphous carbon phase. The crystalline coesite is characterized by vibrational modes showing peaks at 113, 173, 267, and 429 Δcm$^{-1}$, and a strong Si-O mode at 521 Δcm$^{-1}$ (Figure 3.3). The SiO$_2$ glass is characterized by a broad peak near 449 Δcm$^{-1}$, and a substantial drop-off in intensity at 494 Δcm$^{-1}$ (Figure 3.3). Micro-Raman imaging with high spatial resolution indicates that the aggregates of granular coesite are in fact micro-crystallites. Spectra acquired with spot size of 763 nm show both the broad peak near 449 Δcm$^{-1}$ and a strong peak at 521 Δcm$^{-1}$, which is consistent with a mix of coesite plus amorphous SiO$_2$ (Figure 3.4). In some instances, granular coesite contains opaque grains in the center, which display micro-Raman spectra indicative of a carbon phase (i.e, amorphous carbon D and G bands with peaks at 1360 and 1560 Δcm$^{-1}$ (Figure 3.5) (Ferrari, 2007).

3.4.4 NMR Spectroscopy

NMR spectroscopy indicates that the vug silica occurs in several distinct environments that likely include crystalline and two amorphous phases. The spectra (Figure 3.6A) contain a main peak centered near –112 ppm, a broad shoulder near –105 ppm and small, narrow peaks at –108.5 and –114.3 ppm. The $^{29}$Si chemical shift of the second broad peak, –105 ppm, is consistent with a diaplectic silica-rich glass. Based on the NMR results, we estimate that the vug filling consists of 26% coesite, 52% fused silica, and 22% of the second amorphous phase, a densified diaplectic silica glass (see discussion below).

3.5 Discussion

Importantly, interpretation of the SiO$_2$ phases in the vugs requires multiple techniques. Optical petrography and micro-Raman spectroscopy indicate two Si-phases: coesite + SiO$_2$ glass.
NMR spectroscopy, however, indicates three phases: coesite plus two different silica-rich glass phases. Even though the two SiO$_2$ glass phases cannot be distinguished from each other petrographically, they can be distinguished with NMR based on different local chemical environments indicative of different formation mechanisms.

### 3.5.1 NMR Spectroscopy

The $^{29}$Si NMR chemical shifts of the two narrow peaks and their occurrence in near-equal intensity is consistent with previous results reported for crystalline coesite (Smith and Blackwell, 1983), and for coesite present in the Coconino sandstone impactite at Meteor Crater (Yang et al., 1986). A spectrum taken with a 1000 s relaxation delay (data not shown) is essentially identical except for somewhat higher intensity of the narrow peaks. A least-squares fit of the spectrum taken at 100 s relaxation delay (Figure 3.6B-C) yielded peak positions for the two broad peaks of −105 and −112 ppm and widths of 12.6 and 9.3 ppm FWHM, respectively. These large peak widths indicate the signals arise from amorphous substances.

Based on previous work we can propose assignment of the main peak at −112 ppm to amorphous silica. Numerous previous $^{29}$Si NMR studies of fused silica yield a small range of chemical shifts near −112 ppm (e.g., Oestrike et al., 1987; Mahler and Sebald 1995), but with widths generally closer to 12 ppm FWHM (see Malfait et al., 2008 for a summary). For a commercial SiO$_2$ glass, Mahler and Sebald (1995) report a chemical shift of −111.8 ppm and width 9.5 ppm FWHM, values similar to those we observe for the most intense broad peak. In contrast, for quartz recovered from shock experiments up to 38 GPa Fiske et al. (1998) report chemical shifts higher (less negative) than −110 ppm. The width of the peak from deformed quartz increases with increasing shock pressure (Fiske et al. 1998) but is smaller than for the peak at −112 for the present sample. These comparisons indicate that the spectral characteristics of the main peak at −112 ppm more closely resemble those of fused silica than shock-deformed quartz.

The $^{29}$Si chemical shift of the second broad peak, −105 ppm, is consistent with either diaplectic silica-rich glass or an alkali aluminosilicate glass. For quartz recovered from shock experiments at pressures above 30 GPa, Fiske et al. (1998) observe a second peak at higher chemical shifts that was assigned to diaplectic glass, in addition to the signal from deformed quartz. For example, quartz subjected to 33 GPa shock loading yielded $^{29}$Si NMR peaks at −109.9 ppm
for deformed quartz and a broad shoulder at −107.8 ppm for diaplectic glass. For $^{29}$Si NMR, higher (less negative) chemical shifts correspond to smaller average Si-O-Si bond angles, consistent with denser material. Fiske et al. (1998) also report that a fused silica sample that had been statically compressed to 18 GPa at ambient temperature yields a $^{29}$Si chemical shift of −105.6 ppm, consistent with the idea that densified silica-rich glass is characterized by higher $^{29}$Si NMR chemical shifts. Framework alkali aluminosilicate glasses can also yield $^{29}$Si NMR chemical shifts similar to that of the smaller broad peak (Oestrike et al., 1987), for example −104.9 ppm for glass of approximately equimolar albite-orthoclase-silica composition. In this case the higher chemical shift compared to fused silica results from Al substitution in the tetrahedra adjacent to and corner-shared with the silicate tetrahedron. This overlap of chemical shift ranges for different materials prevents the nature of the second amorphous phase from being determined solely from its $^{29}$Si NMR chemical shift. However, absence of a significant $^{27}$Al MAS/NMR signal from the sample indicates that Al is not a major component, thereby allowing us to rule out the possibility of this being an aluminosilicate glass.

Estimation of the relative proportions of the three detected phases is complicated by clear evidence for differential relaxation effects between the crystalline coesite and the amorphous phases. The coesite peaks represent 3±1 percent of the integrated intensity in the spectrum taken with a 100 s relaxation delay and 5±1 percent for that at 1000 s. This relative increase is similar to, but somewhat smaller than the factor of two increase observed by Myers et al. (1998) for coesite in an NMR relaxation study of the Coconino sandstone. That study found that complete relaxation of the coesite $^{29}$Si NMR signal required approximately 20,000 s, and that at 1000 s the signal had recovered to 22% of its equilibrium value. Assuming the present sample exhibits similar relaxation properties and that the amorphous phases are fully relaxed at 1000 s, we estimate that approximately 26% of the Si occurs in coesite. The smaller differential relaxation we observed from 100 to 1000 s compared to Myers et al. (1998) suggests that the relaxation rate is faster for the present sample, in which case this estimate represents a maximum value for the abundance of coesite. Relaxation rates are highly dependent on the impurity concentration, so accurate proportions require acquisition of fully relaxed spectra that is impractical for the presently available amount of sample. The ratio of integrated intensity of the two broad peaks does not change appreciably from 100 to 1000 s of relaxation, giving values of 2.39 and 2.35. This similarity suggests that both signals are nearly fully relaxed at 100 s, because it is unlikely for separate phases
to yield nearly identical relaxation rates. Given these estimates and caveats, we estimate that the
vug filling consists of 26 mol percent coesite, 52 mol percent fused silica, and 22 mol percent of
the second amorphous phase, interpreted to be a densified diaplectic silica glass.

3.5.2 Texture and formation conditions

The coesite at Lonar exhibits an unusual texture: concentration of granular coesite along
pre-impact vesicle walls (as an apparent rind) and in densely packed regions near or at the center
of the SiO$_2$ glass. There are multiple possible explanations for this texture: 1) concentration of
stress (or P, and T) at the edges and center of the vug due to interactions between the shock wave
and the vesicle wall/vug; 2) nucleation of coesite against the vesicle wall; and/or 3) impurities or
heterogeneities within the glass serving as a nucleation point for coesite. The extreme
heterogeneity among vugs in these samples suggests it is likely that all three possibilities are
contributing to the texture of the coesite at Lonar. Shock waves are known to refract when passing
through geologically complex materials (Sharp and DeCarli, 2005; Kieffer et al., 1971) and there
is likely a great contrast between the basalt and vug (particularly if the filling is opalline silica).
Generally speaking, nucleation fronts are also common -- particularly along surfaces that serve as
energy minima for initiation of crystallization. Lastly, in these samples, we see an uneven
distribution of carbon phases (Figure 3.7), which suggest there is a heterogeneous distribution of
impurities, and these impurities are frequently the site of nucleation of the coesite (Figure 3.2E).

Our work highlights the importance of technique when interpreting glass components
within impact samples. In impact settings, glass can be produced in two ways – as a solid-state
transformation (i.e., diaplectic glass) or as a fused glass. The formation conditions of these glass
types are different and there are important geochemical and structural differences between fused
glass and a glass formed by solid-state processes. As shown by our data, relying on optical
petrography or Raman spectroscopy alone may not be sufficient to interpret exact formation
conditions.

Coesite at Lonar is found only within former amygdules of the basalts, suggesting the SiO$_2$
precursor phase was a pre-shock secondary phase. Pre-impact alteration and precipitation of
secondary minerals including zeolite, quartz, opaline silica, chalcedony, and tridymite is common
in the target Deccan basalts at Lonar (Sukheswala et al., 1974). The presence of coesite here
represents the first direct observation of a terrestrial shocked secondary mineral. Secondary silica
was suggested as the source for coesite within melt-breccias at the Vredefort impact structure (Martini, 1991), but direct petrographic evidence is lacking.

The presence of coesite in impact materials is often used as an indicator of impact conditions, specifically pressures and temperatures (e.g., French, 1998). However, in these specific samples, shock barometry may be complicated by a series of factors. First, common secondary minerals in the Deccan basalts at Lonar include both opaline silica and quartz. Because all the SiO$_2$ present in these samples has been transformed to coesite + glass, it is not possible to determine the starting pre-shock SiO$_2$ phase. The specific starting phase likely affects exact formation conditions. For example, it is common for experimental studies of coesite to start with amorphous SiO$_2$ because synthesizing coesite from an amorphous material rather than quartz is energetically more favorable. Similarly, addition of Si-OH changes formation conditions of coesite (Zhang et al., 2008), and water content is known to change the conditions under which coesite can form in impact settings (Osinski, 2007).

Even if we assume that the coesite forms as a replacement after quartz, the specific P-T conditions remain unclear. Currently, there is debate as to how coesite forms in impact settings – as either a solid-state transformation (Stoffler, 1971; Ferrierè and Osinski, 2013) or as the crystallization from a melt (Chen et al., 2010). The texture of the coesite in these Lonar basalt samples, particularly the isolated granular coesite within the glass, is consistent with textures at the Xiuyan impact structure, which Chen et al. (2010) interpret as having crystallized from a melt. Also consistent with this is the micro-crystallites, which appear to be nucleating (in some instances against a carbon phase; Figure 3.2E; Figure 3.5). Secondary Electron images in the FIB show granular coesite is an aggregate of sub-micron grains embedded within the glass. Textures of the nano-crystallites suggest nucleation from a rapidly quenched melt (Figure 3.8).

Furthermore, our NMR data suggests at least one of the glass phases is a fused silica glass, so interpreting the coesite as crystallizing from a melt is not unreasonable because our NMR results would seem to require that at least one of the two SiO$_2$ glasses is a melt product. This is based on the lack of compositional difference between the two detected amorphous phases.

Impact melt, however, is not consistent with the bulk texture of this sample. This sample is classified as shock Class 2 (Kieffer et al., 1976; Wright et al., 2011; Jaret et al., 2015), defined by the presence of maskelynite, which lacks flow texture. Importantly, preservation of zoning in
the maskelynite and the presence of remnant anisotropy in the maskelynite indicates that the plagioclase was transformed to glass via solid-state transformations (Jaret et al., 2015).

We can reconcile this discrepancy between the SiO$_2$ phases suggesting formation from a melt and bulk-rock textures of the solid-state maskelynite by considering the petrographic context of the SiO$_2$ phases. In these samples, coesite occurs only within pre-impact amygdules, and thus we interpret these as areas of extremely localized melting associated with the vesicle.

Analysis of experimentally and naturally shocked porous sandstones has shown that during shock, collapsing pore-space can cause localized increases in pressure and temperature and can trigger local melting, as suggested for the Coconino Sandstone at Meteor Crater (Keiffer et al., 1971). Similarly, at Vredefort, coesite is associated with melt within pseudotachylite, and are interpreted to have formed due to local heating associated with collapsing fractures during shock. Grain-boundary interactions between the shock wave, individual grains, and pore space cause localized concentrations of stress (and pressure and temperature) at grain margins, such that shock events in porous rocks deposit more energy than in non-porous materials (Keiffer et al., 1971). The samples from Lonar studied here are not exactly like porous sandstones, but a similar process may occur due to collapsing space within and adjacent to the vesicle.

The association of melt with high-pressure polymorphs in impact settings may be more widespread than previously recognized. Interestingly, at Bosumtwi, some coesite inclusions in diaplectic SiO$_2$ glass occur in grains that are directly adjacent to melt (Morrow, 2007), and the coesite formation may indeed be tied to heating from adjacent melt. A similar phenomenon occurs with high-pressure feldspar phases in meteorites where those high-pressure phases occur in association with melt veins and pockets, as has been suggested for the formation of tissintite (Walton et al., 2014).

At Lonar, the local melting is not associated with fractures, but instead vugs, which may provide a new opportunity to look for high-pressure phases. If collapsing vesicles or concentration of stress as the shock wave interacts with the vesicles and fillings generate heat during shock, as suggested here, then one might expect to find similar evidence of melt or high pressure phases in shocked vesicular meteorites or terrestrial impacts into vesicular targets.

3.6 Conclusions
Here we present the first observation of coesite at the Lonar crater and address its significance. Coesite is confined to within former silica amygdules in the target vesicular basalts. This work is also the first report of high-pressure phases found in a shocked secondary precipitate. The coesite occurs as 30 – 40 µm aggregates of smaller crystallites, interpreted as having crystallized directly from a melt. $^{29}$Si NMR results suggest the coesite occurs in association with two distinct silica-rich glass phases, one of which is a quenched melt (at low P). Impact-melting, however, is inconsistent with the bulk rock textures, which show no large-scale flow textures and these sample contain maskelynite grains, which preserve original igneous zoning, and Infrared anisotropy. We reconcile these discrepancies by the petrographic context of the coesite and silica fused glass, which are confined only to the vesicles. Therefore, we suggest extremely localized melting, caused by collapsing vesicles during shock.
Figure 3.1: Structures with reports of coesite. Structures with reports of coesite that include petrographic context are shown in red boxes. All are modified after L. Ferrière (http://www.meteorimpactonearth.com/meteorite.html) References used are listed in Table 1.
Figure 3.2: Lonar coesite. A) Hand sample. Coesite occurs within the bright white amygdules (yellow arrows). Scale is in mm. B and D) plane-polarized light images (slightly thicker than standard thin-section thickness) showing granular coesite within the amygdule and as well as a rind of coesite at the edge of the amygdule (red arrow). C, E, F). Coesite is the green-yellow and commonly forms granular textures E) Granular coesite which contain dark, amorphous carbon centers (blue arrow). F) Granular coesite within SiO$_2$ glass. Position of this image is marked by the box in D.
Figure 3.3: Raman spectra of A) coesite and B) SiO$_2$ glass.
Figure 3.4: Raman map (A) and spectra of SiO$_2$ glass (B), coesite (C), and a mix of coesite + glass (D). Locations of spectra are indicated by associated letters.
Figure 3.5: Raman map (A) and spectra of coesite with dark opaque centers (B). The centers are amorphous carbon, as indicated by the D and G Raman bands.
Figure 3.6: $^{29}$Si MAS/NMR spectrum of silica-rich amygdale, showing the presence of peaks for coesite (narrow peaks) and two amorphous phases (broad peak near –112 ppm and broad shoulder near –105 ppm). (A) Observed spectrum acquired at a spinning rate of 12 kHz and a 100 s relaxation delay for a total of 4176 acquisitions. (B) least squares fit of the spectrum in (A) composed of four Gaussian peaks (C).
Figure 3.7: SEM image (A) and map (B) of carbon-rich SiO$_2$ glass and coesite.
Figure 3.8: Focused Ion Beam slices of coesite + glass. A) Secondary Ion Image of polished slab. B) Transmitted light image of the FIB foil mounted on a needle. In both instances the granular texture of the coesite is visible.
Figure SI 1: $^{29}$Si MAS/NMR spectra of silica-rich vesicle filling taken at different relaxation delays as indicated. Spectra acquired with 4 us pulses ($\pi/2$) at a 12 kHz spinning rate for a total of 414 (1000 s), 4176 (100 s), and 142,704 (s) acquisitions.
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<td>Ohtani et al 2011</td>
<td>granular coesite. Rounded aggregates of up to 300 nm</td>
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<td>Miyahara et al., 2014</td>
<td>granular coesite. Some are adjacent to melt veins</td>
<td>Raman spectroscopy and TEM</td>
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3.8 References


Lee, S. K., S. Y. Park, H. I. Kim, O. Tschauer, P. Asimow, L. Bai, Y. Xiao, and P. Chow,


Chapter 4
What Argon Ages of Maskelynite Mean and Don’t Mean: Implications for Martian Meteorites

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4.1 Introduction

Many of the fundamental questions of martian geology would benefit from absolute chronology. Although there have been attempts to obtain absolute ages directly on Mars (Farley et al., 2014), high precision martian geochronology measurements are presently best obtained from samples in terrestrial laboratories, specifically the martian meteorites. These meteorites have experienced violent and complex histories, having been involved in at least one large impact event. How impacts affect radioisotopic chronometers has been the topic of much debate (e.g., Bouvier et al., 2009, 2008; Stephan and Jessberger, 1992), and therefore the interpretations of ages obtained from shocked meteorites have been contentious. In the study presented here, we use $^{40}\text{Ar}/^{39}\text{Ar}$ analyses of unshocked plagioclase, impact melt, and maskelynite from in and around the Manicouagan impact structure, Canada, to examine the $^{40}\text{Ar}/^{39}\text{Ar}$ system in shocked material from a known event with known target rock geology. Our results show that maskelynite yields apparent ages that are intermediate to the target and impact age. Thus, their apparent ages are not meaningful, but the results show they are demonstrably partially degassed by the shock.

Current absolute age estimates for martian samples range from ~150 Ma to more than ~4.3 Ga (Bouvier et al., 2009, 2008; Nyquist et al., 2001). K-Ar analysis by the Curiosity rover of the Sheepbed mudstone yield an age of 4.21 Ga (Farley et al., 2014). The orthopyroxenite martian meteorite ALH84001 has a crystallization age of close to 4 billion years (Lapen et al., 2010; Nyquist et al., 2001). Naklites and Chassignites give ages of 1.4 Ga (Korochantseva et al., 2011). U-Pb ages from zircons within the “Black Beauty” breccia yield ages of 4.4, 1.7, and 1.4 Ga (Agee, 2014). The shergottites, which make up the majority of martian meteorite collection, however, yield younger and more varied argon ages, between 150 and 500 Ma (Nyquist et al., 2001). These meteorites have experienced moderate shock levels, with majority of plagioclase converted to maskelynite. Additionally, these samples have discrepancies between chronometers, such as Sm-Nd or Rb-Sr, used for the same samples, which has led to the suggestion that the “young” argon ages date a resetting event, presumably by impact or aqueous processes (Gaffney et al., 2011).
Shock resetting of the K-Ar system, however, is a controversial topic. During impacts, deformation occurs in two fundamentally different ways: thermally controlled processes (e.g., impact melting) and isochemical, pressure dominated changes (e.g., formation of high pressure polymorphs and the development of diaplectic glasses). Impact melts are known to yield ages consistent with the time of impact (Scharer and Deutsch, 1990; Young, 2014). Resetting of the K-Ar system is predominantly understood as a thermal process, and shock-deformed, but unmelted material has been thought to be resistant to argon resetting. Much of this assumption comes from shock experiments, which show no change in the behavior of the K-Ar system up to shock pressures of 52.5 GPa (Jessberger and Ostertag, 1982; Stephan and Jessberger, 1992). As we will show here, naturally shocked samples behave differently than experimentally shocked samples with respect to their argon isotope systematics.

4.2 Samples

The samples used in this study are from the Manicouagan impact structure, Canada. Manicouagan is an 80 km-diameter impact structure formed within predominantly 0.8 – 1.0 Ga Grenville terrain rocks. Over the last decade Manicouagan has been the subject of a focused research program directed at better understanding the impact process and linking the crater as an analogue site with impact structures on other planetary bodies, such as those on the Moon and Mars (Spray et al., 2010). Notably, Manicouagan has been the focus of extensive dating studies. Our study uses mineral separates from three source lithologies: unshocked country rock, impact melt, and shocked country rock (Figure S1). Unshocked samples were collected from Mont Brilliant garnet-bearing meta-anorthosites exposed in the NNW of the structure, where plagioclases are labradorite in composition and 0.25 - 1 mm in size. Impact melt samples were collected from Observation Lake and are medium-to-fine grained quartz monzodiorite. The maskelynite samples were collected from Mont de Babel and Maskelynite Peak, within the central uplift. They are coarse-grained anorthosites (>1 mm), where the plagioclase (labradorite) has been converted to maskelynite.

Critical to the discussion of argon resetting is understanding whether the maskelynite was formed via melting, or by direct solid-state transformation to glass. There is considerable debate over the formation mechanism of maskelynite (Diemann and Arndt, 1984; El Goresy et al., 2013; Jaret et al., 2015; Stöffler, 1971). Here we follow the methods of Jaret et al. (2015) and use the
presence of infrared anisotropy within the maskelynite as indicative of formation via solid-state processes (Figure S2). This work demonstrated that while maskelynite displays infrared and X-ray anisotropy, impact melt glass does not. Although the sample is amorphous, the peak position of the Si-O stretching vibration near 1000 cm$^{-1}$ changes slightly with orientation, suggesting this grain transformed without homogenization or melting (i.e., a diaplectic glass formed by shock, see Jaret et al., 2015).

4.3 $^{40}$Ar/$^{39}$Ar Results

We analyzed two samples of the unshocked country rocks, (Figure 4.1A, Table 1). Both samples show somewhat disturbed spectra, with integrated ages of 838 ± 3 and 877 ± 16 Ma. One sample does define a plateau age of 847 ± 10 Ma (MSWD = 0.92). Both age spectra are consistent with a Grenvillian target rock age, and likely represents cooling from high-grade metamorphism during the Grenville, as these samples have Sm-Nd and U-Pb ages of 1.5 Ga (Thomson, 2009). Single-step total fusion analyses from plagioclase within the impact melt rock indicate a well-behaved system as shown by the age probability diagram (Figure 4.1B), with an age of 216.52 ± 0.16 Ma (MSWD = 1.97). Two analyses have low $^{39}$Ar (shown in red), and were not included in the age calculations, but are shown here for completeness. When plotted on an inverse isochron diagram (Figure 4.1C), melt samples indicate a slightly elevated initial $^{40}$Ar/$^{36}$Ar of 305 ± 5, yielding an age of 215.6 ± 0.9 Ma. Taking the trapped initial $^{40}$Ar/$^{36}$Ar into account, the best estimate of the age of the impact of 215.6 ± 0.16 Ma.

Step heating analysis of the maskelynite yields an intermediate result between the terrane and impact ages, with an integrated age of 513 ± 8 Ma. There is a general correlation between apparent age and both $\%^{40}$Ar* and the Ca/K, where steps with younger ages have both lower $\%^{40}$Ar* and Ca/K, The last step (the final 20% of released $^{39}$Ar) has lower $\%^{40}$Ar*, lower Ca/K, and a younger apparent age. Single-step total fusion ages of maskelynite (black circles in Figure 4.1D) are variable, but also yield results between 450 and 600 Ma, and thus consistent with the range of ages of steps from the step heating analyses.

When plotted on an isochron diagram (Figure 4.2A), maskelynite samples (individual steps and total fusion data) are clearly scattered, but fall near a 500 Ma reference isochron. The results are entirely contained between modern atmosphere, and end-members representing the target rocks ($^{40}$K/$^{40}$Ar* for and 800 Ma rock) and the impact ($^{40}$K/$^{40}$Ar* for a 215 Ma rock).
4.4 Discussion

Our measurement of the age of the target rocks at Manicouagan is ~847 Ma, consistent with their location within the Grenville target terrain. This age is slightly younger than the previous K-Ar age estimate of 932 ± 7 Ma (Wolfe, 1971), but given the relatively low closure temperature of the argon system in feldspar, some dispersion in the country rock from the pre-impact geologic history is to be expected. Given that this sample location is not well documented, I am not sure that the measurement was made on the same sample, and argon ages within 100 Ma are not unheard of for Grenville units. We interpret the time of impact to be 215.6 ± 0.16 Ma as indicated by the impact melt. This age is within error of previous estimates of the Manicouagan impact, including (1) the high-resolution ID-TIMS age of 215.5 Ma from zircons (Ramezani et al., 2005) within the same sample we measured, (2) U-Pb zircon age of 214 +/- 1 Ma (Hodych and Dunning, 1992), (3) (U-Th)/He age from impact melt sheet zircons of 213.2 +/- 5.4 Ma (Van Soest et al., 2011), and (4) age from titanites from the central uplift of 208.9 +/- 5.1 Ma (Biren et al., 2014).

The apparent ages of the maskelynite do not match either the impact age or the target age, but instead they are intermediate and of no geological age significance. Importantly, in addition to their non-meaningful ages, the step heating experiments do not show the typical age-release spectrum of rocks that have undergone thermal metamorphism, although they are quite scattered (Figure 4.2B). Regional metamorphic resetting, which is a slow, temperature-dominated process, affects sub-grain domains differently depending upon the size and crystallographic structure of the domains and their argon retention abilities. This typically leads to a stepped age spectrum, with lower temperature steps yielding younger apparent ages due to preferential argon loss within those domains (Blue curve, Figure 4.2B). Manicouagan maskelynite samples, however, do not show correlation between subgrain domain and apparent age, but instead appear to have partially lost argon relatively uniformly across all domains (Black curve, Fig. 2B). This is likely a direct shock effect in response to the extreme pressure pulse experienced by these samples upon impact. It also appears that the resetting may not be homogeneous across the entire sample. It would not be possible to determine the age of the target rock or the impact event from these measurements. This suggests that the maskelynite has undergone some argon loss during shock, but in a manner that is fundamentally different from thermal metamorphic resetting.
Individual single-step total fusion ages of maskelynite give a range of ages spanning between 400 Ma and 600 Ma. Similar scatter and ages were seen in the K-Ar analyses of Wolfe (Wolfe, 1971), and interpreted as a mixing of the end-member target and impact ages.

As shown from the $^{40}\text{K}/^{40}\text{Ar}$ vs. $^{36}\text{Ar}/^{40}\text{Ar}$ isotope correlation diagram (Figure 4.2A) the maskelynite data lie entirely within the triangle formed between the target and impact end-members and modern atmospheric argon ($^{40}\text{Ar}/^{36}\text{Ar}$ of 298.5). As seen with the age release spectrum (Figure 4.1), the maskelynite does not show a systematic increase in age with heating steps that would be associated with partial resetting during metamorphic resetting. In other words, from the maskelynite data alone, it would not be possible to tell that these samples were disturbed at 215 Ma.

We suggest an analogous result has been found in maskelynite from martian meteorites, where maskelynite grains from within the same rock yield ages that differ from each other by as much as 100 Ma, and where the $^{40}\text{Ar}/^{39}\text{Ar}$ ages of the maskelynite grains do not match those of other chronometers applied to the same meteorites (Nyquist et al., 2001). In the last decade, there has been growing interest in the interpretation of the argon ages of martian meteorites (Walton et al., 2014), and it has been suggested that $^{40}\text{Ar}/^{39}\text{Ar}$ ages are not reliable. Our results go even farther to imply that argon ages obtained from maskelynite may reflect some intermediate composition that is neither the impact age nor the target age.

These results differ from what has been reported before based on shock experiments, which showed plagioclase to be highly resistant to shock resetting (Stephan and Jessberger, 1992). The most likely explanation for this discrepancy is that shock experiments are predominately focused on reproducing shock pressures and do not adequately simulate the associated thermal pulse of a natural impact. Alternatively, the lack of resetting in shock experiments could be due to differences in timescales of shock experiments and natural shock events. Shock experiments have typical pulse durations of <1 µs, whereas natural impacts have typical pulse durations of 1s (Langenhorst, 2002). Because resetting of argon is fundamentally diffusion-based, either the increased temperature or increased time of natural impacts could be contributing to the shock resetting. This could be evaluated in detail by looking at Arrhenius plots, but we did not collect this data. While this is commonly done in the terrestrial community, Arrhenious plots have rarely been applied to impact or meteorite data (Cassatta et al., 2011). Interestingly, even though they did not see differences in ages between shocked and unshocked samples in their experiments,
Stephan and Jessberger 1992, did see changes in the diffusion rates, and have suggested that this could lead to partial resetting in naturally shocked samples.

4.5 Conclusions

Based on our results from Manicouagan, it appears that maskelynite is not a reliable phase for $^{40}\text{Ar}/^{39}\text{Ar}$ chronology. The calculated ages obtained from maskelynite do not reflect the timing of any known geologic event at Manicouagan. This suggests that $^{40}\text{Ar}/^{39}\text{Ar}$ ages from maskelynite in martian samples also are not likely to be a direct measure of geologic activity on Mars. Instead, these ages could serve as minimum ages for the crystallization of these rock and maximum ages for the time of impact shocking. Argon ages for shergottites span a large range from $\sim$100 Ma to $\sim$500 Ma (Korochantseva et al., 2009; Nyquist et al., 2001). Some of this scatter appears to be phase dependent, where maskelynite ages tending to yield older ($\sim$400-500 Ma) ages (Korochantseva et al., 2009). Recently, argon ages of clearly vesiculated plagioclase composition impact melt in Dhofar 378 and NWA 4797 have yielded argon ages of 141 Ma (Park et al., 2008), and as young as 45 Ma (Walton et al., 2014). Because these studies clearly showed they were sampling impact melt, these young ages cannot be considered to reflect the crystallization age of the shergottites. Our results suggest that the $\sim$500 Ma ages from shergottie maskelynite are likely representing partial resetting and therefore is a minimum age for crystallization of the shergottites. The impact event would have been more recent -- either a melting event as suggested by Walton et al. (2014) the ejection event, some later heating event unrelated to impacts, or some combination of these.

4.6 Supplemental Material

4.6.1 Sample Preparation

For all samples, individual plagioclase grains were separated from the host rock. Unshocked target rocks were crushed by hand. Maskelynite was either crushed by hand or disaggregated using the SelFrag electronic-pulse disaggregation system at Lamont. Melt-rocks were disaggregated with the SelFrag. For xenocrystic grains, clasts were first cut out of the melt-breccia, and the edges were ground by hand to remove any melt. Then, the clasts were disaggregated with the SelFrag.
For each sample, individual grains were mounted on double-sided tape for micro-Raman analyses. Plagioclase from the impact-melt rock were small and in order to obtain radiogenic argon, multiple grains were analyzed together. To ensure grains grouped together were the same composition and structure, grains were mounted on double-sided tape and analyzed with micro-Raman spectroscopy. Grains were grouped based on similar Raman spectra.

Additional, doubly-polished thin sections of each sample were prepared for optical petrography and micro-Raman spectroscopy.

4.6.2 Micro-Raman spectroscopy

We collected micro-Raman spectra using a WiTec alpha300R confocal imaging system, system in the Center for Planetary Exploration at Stony Brook University. It is equipped with a 532 nm Nd YAG laser through a 20X (0.45 NA) objective with a spot size of (1.41 µm). Each spectrum was acquired with a laser power of 2.25 mW and consisted of 60 acquisitions each with a 1 sec integration time. For larger grains (> 250 µm) 2 or 3 spectra were acquired per grain.

4.6.3 Micro-FTIR spectroscopy

We collected micro-FTIR point spectra of single grains in thin section using a Nicolet iN10MX FTIR microscope, in the Center for Planetary Exploration at Stony Brook University. This instrument is equipped with a liquid nitrogen-cooled HgCdTe array detector capable of acquiring hyperspectral image cubes between 715 and 7000 cm\(^{-1}\) (1.4-14 µm) at 25 µm/pixel spatial sampling. To test for preservation of orientation effects, multiple grains were measured with the assumption that the thin section captures a random sampling of grain orientations (Jaret et al., 2015).

4.6.4 \(^{40}\)Ar/\(^{39}\)Ar analyses

Samples were separated and feldspar grains were hand-picked and measured with micro-Raman spectroscopy (as described above). Grains selected for argon analyses were co-irradiated with Fish Canyon and Fire Clay sanidine monitors for 8-hours at the USGS TRIGA reactor in Denver, CO. Interfering isotopes produced by nucleogenic reactions during irradiation were corrected using the production ratios of Dalrymple et al. (1981), specifically:

\[
(39/37)\text{Ca} = 7.11\text{e-}4; \quad (38/37)\text{Ca} = 3.29\text{e-}5; \quad (36/37)\text{Ca} = 2.81\text{e-}4; \quad (38/39)\text{K} = 1.314\text{e-}3;
\]
Analyses were made on either single-step total fusing analyses using a CO$_2$ laser, or step-heating experiments where samples were encapsulated in Ta tubes and heated incrementally with a diode laser. For step-heated samples, multiple grains were loaded for each experiment. In some cases, because of the low abundances, these grains were taken from multiple irradiation pits. All samples that were grouped together for step heating were irradiated in the same irradiation level. The released gases were admitted into an automated extraction system for clean-up (for 300 seconds with the single-step samples and for 660 seconds with the step-heated samples), during which the gases were exposed to Zr-Fe-V metal alloy getters set at 2 amps to strip off reactive gases such as H$_2$, CO, CO$_2$, and N$_2$, leaving only the inert gases. The remaining noble gases were admitted into a VG5400 mass spectrometer system equipped with a modified Neir ion source, and isotopic measurements were collected by peak hopping in static mode using an analogue multiplier with a sensitivity of 3.5x10$^{-14}$ mol / nA.

Decay constants used are 5.72E-11 and 8.8E-13. We used 2 monitor standards: the internationally accepted Fish Canyon (28.201 +/- 0.046 Ma, (Kuiper et al., 2008) and an internal standard, the Fire Clay Tonstine (using the zircon age of 315.25 +/- 0.55 as the age (Shea et al., in prep). We report the ages calculated using the Fire Clay Tonstine as a monitor because this age (315 Ma) is significantly closer in age to the age of the Manicouagan impact event. The apparent age of Fish Canyon with this approach is 28.38 +/- 0.10 Ma at the time of the measurements. Detailed investigations of intercalibration and use of different monitor standards is ongoing and will be presented in a future paper.
Figure 4.1: Argon isotope results. A) Ca/K, $\%^{40}Ar^*$, and age spectra of the unshocked anorthosite target rocks. There is some scatter between the two samples, but both yield Grenvillian ages. B) Age probability histogram for plagioclase within the impact melt rocks. Two analyses (plotted in red) have low $\%^{40}Ar^*$, and were excluded from the age calculation, but are shown here (dotted curve) for completeness. C) Inverse isochron from plagioclase in the impact melt (same analyses as plotted in B). The isochron shows a wide range of $\%$ radiogenic $^{40}Ar$ indicates a slightly elevated initial $^{40}Ar/^{36}Ar$ of $305 \pm 5$, and an age of $215.6 \pm 0.9$ Ma.) Ca/K, $\%^{40}Ar^*$, and step heating age spectra for the maskelynite. With the exception of the final step, the integrated calculated age of the maskelynite is $513 \pm 8$ Ma. Results from single-step fusion of individual grains (black circles on far left) are scattered, but fall within the range of the steps-heating ages.
Figure 4.2: Comparison of isotopic data for impact melt, maskelynite, and target rocks highlighting the mixing and partial resetting seen in the maskelynite. A) $^{40}$K/$^{40}$Ar vs $^{36}$Ar/$^{40}$Ar isotope correlation diagram. Endmembers (circles) include modern atmosphere (blue), $^{40}$K/$^{40}$Ar of Grenville target rocks, and $^{40}$K/$^{40}$Ar of the time of impact (215 Ma). Reference isochrons at 1000 Ma, 500 Ma and 100 Ma are shown in grey. Both the impact melt samples (orange diamonds) and the unshocked target rocks (green squares, does not include the first 3 heating steps where there appears to be some excess $^{40}$Ar* define isochrons. The maskelynite data scatter near a 500 Ma isochron and appears to record partial degassing of the Grenville target at the time of impact. If it were not affected, it would plot with the unshocked Grenville data. If it were completely reset, it would plot with the feldspars from the melt rock.

B) Schematic idealized age release spectra showing expected patterns for rocks completely degassed at 800 Ma, representing Grenville target rocks (green) and rocks completely degassed at 215 Ma, representing impact melt (orange). The blue curve shows one likely pattern for Grenville rocks that were partially reset by thermal metamorphism at 215 Ma. The black curve shows the pattern of the maskelynite, suggesting that the partial loss due to shock is not domain specific yielding a highly scattered age-release spectrum with all steps showing intermediate ages.
Figure S1: Location of the Manicouagan impact structure, Quebec, Canada; b) Simplified geological map of the Manicouagan impact structure, after Thompson and Spray (Thompson and Spray, 2017) with the sample locations used in this study: 1 – unshocked anorthositic gneiss, 2 – shocked anorthositic gneiss, and 3 – impact melt rock.
Figure S2: Micro-FTIR reflectance spectra of 2 orientations in the maskelynite. Both orientations show one broad peak indicative of an amorphous plagioclase glass, but the specific position of the peak changes with orientation. We interpret this to suggest the maskelynite deformed via solid-state processes (Jaret et al., 2015).
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| 2 C    | 3.4962915   | 0.019779             | 0.0001573              | 6.93E-05            | 0.001527               | 1.81E-05            | 0.000323               | 0.000178             | 0.000893                |
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| 2 J    | 18.120386   | 0.020058             | 0.0092388              | 7.29E-05            | 0.001156               | 1.92E-05            | 0.008363               | 0.000532             | 0.0003067               |</p>
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**Single Steps**

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4.7 References


Ramezani, J., Bowring, S.A., Pringle, M.S., Winslow, F.D., Rasbury, E.T., 2005. The


Chapter 5
Spectroscopic and Petrographic Comparison of Experimentally Shocked Albite, Andesine, and Bytownite

This chapter has not been submitted yet but is being prepared for submission in the Journal of Geophysical Research: Planets

5.1 Abstract
Here we have characterized experimentally shocked albite, andesine, and bytownite using optical petrography, micro-Raman, and micro-FTIR spectroscopy. Feldspars are a common mineral on the surfaces of the Moon and Mars, as well as present in meteorites, and so understanding their spectroscopic response to shock is important for interpretations of remote and returned samples from these bodies. Across all techniques, we show that the specific composition of feldspars affects shock deformation, where more Ca-rich feldspars transform at lower shock conditions than more Na-rich feldspars. Complete amorphization, a major transformation in shocked feldspars, occurs between 50.0 and 55.8 GPa for albite, between 28.4 and 29.4 GPa for andesine, and between 25.5 and 27.0 for bytownite. Petrographically, these experimentally shocked samples do not exhibit the traditional planar microstructures common in naturally shocked feldspar, despite showing the expected trends of internal disordering and deformation as seen in the micro-Raman and infrared spectra. Additionally, these samples are highly heterogeneous and suggest that shock heterogeneity is an important factor to consider when dealing with micro-scale characterization of shocked materials.

5.2 Introduction
Impact cratering is a ubiquitous geological processes in the Solar System. The surfaces of all terrestrial planets and asteroids have undergone many impact events. On the Earth, the effects of impact cratering are less obvious, where many of the ~190 known impact craters have been obscured by other geologic processes, such as burial, erosion, or plate tectonics. During impact events, the hypervelocity collision between an impactor and the planetary surface drives a shock wave into both the target and the impactor, leaving a suite of deformation effects (Melosh, 1989, French, 1998). Collectively referred to as impact metamorphism (or shock metamorphism when referring to specifically the deformation related to the shock wave), this process results in
brecciation, melting, formation of high pressure, high temperature polymorphs, and other mineral-scale crystallographic transformations. These effects occur over a range of pressure intervals for different minerals, as originally documented by optical petrography observations of planar deformation features (PDFs), amorphization, and melting (e.g., Bischoff and Stöffler, 1992; Langenhorst, 1994; Sharp and Decarli, 2006; Stöffler, 1971). Optical petrographic classifications of shock stages in experimentally shocked minerals typically constrain the peak pressure bins to relatively coarse precision (10-25 GPa; e.g., Bischoff and Stöffler, 1992; Kieffer et al., 1976; Stöffler, 1971). However, Raman and thermal infrared vibrational spectroscopy techniques have been used to document systematic changes in the strength and position of absorption bands with pressure that are associated with progressive amorphization, particularly in shocked plagioclase feldspars (Fritz et al., 2005; Heymann and Horz, 1990; Johnson et al., 2003, 2002). In this work we use microscopic thermal infrared and Raman techniques to probe the crystalline structure of plagioclase feldspars, a major component of basaltic planetary surfaces. By analyzing the small-scale spectral and petrographic variability seen in thin sections made from a suite of experimentally shocked albite-, andesine-, and bytownite-rich rocks (Johnson, 2012; Johnson et al., 2003, 2002), we can quantify how shock metamorphism alters individual mineral grains in the context of their surroundings. Such information is vital in understanding the spectral variations observed in naturally shocked samples, where pressure pulses are about $10^3$ times longer in duration than in lab experiments. Indeed, the shock pressure at the front of a propagating shock wave can vary greatly within an individual grain, among nearby grains, or along grain boundaries, with corresponding local variations in temperature. Examination of the spectral effects of shock pressures and shock propagation at the level of these individual grains requires spectroscopy with high spatial resolution. Furthermore, studying natural and experimentally shocked samples also can provide context for features that are observed in meteorites, offering new means of interpreting the histories of their asteroid parent bodies. For example, the Curiosity rover on Mars has documented significant amounts of amorphous material in the sedimentary deposits at Gale Crater (Dehouck et al., 2014), which has been interpreted to be either volcanic, diagenetic, or impact-related. Understanding if impact amorphous material can be distinguished from amorphous material formed by other processes (and if so, which tool to use to best identify them) would useful to future missions or studies of returned samples.

5.3 Background
Most of the early work on shock metamorphism focused on transformations of silicates, specifically quartz and feldspars (Ahrens et al., 1969; Chao, 1968; Huffman and Reimold, 1996; Jaret et al., 2015; Stöffler, 1971; von Engelhardt and Stoffler, 1968). While the work presented here work focuses exclusively on plagioclase feldspars, it is worth noting that many of the models and ideas of how shock affects feldspar are based heavily on analogy with the well-studied shock effects in quartz. Detailed reviews of shock metamorphic effects in framework silicates can be found in (Alexopoulos et al., 1988; Chao, 1968; Ferrière et al., 2009; Ferrière and Osinski, 2013; Grieve et al., 1996; Short, 1966; von Engelhardt and Stoffler, 1968).

The effects of shock in feldspars are progressive (Jaret et al., 2014; Kieffer et al., 1976; Stöffler, 1971): the appearance of PDFs, the formation of diaplectic glass, and finally, whole scale melting. Based on the petrographic trend of shock textures in quartz, several classification schemes for assessing shock level in natural samples have been developed (Chao, 1968; Singleton et al., 2011; Stöffler, 1971; von Engelhardt and Stoffler, 1968). Pressures of formation have been estimated for the transition to amorphous material, and are typically calibrated based on shock experiments (Horz and Quaide, 1973; Huffman et al., 1993; Ostertag, 1983; Stöffler, 1971; von Engelhardt and Stoffler, 1968).

Shock textures in feldspars are more complicated than in quartz. In addition to PDFs, feldspars (particularly alkali feldspars) exhibit twin-plane dependent textures. That is, PDFs frequently occur only within alternating twin planes, but adjacent twins are deformation free. In albite, this has been interpreted to be due to the orientation difference between adjacent twins. Such alternate-twin features are also seen where every other twin has been converted to diaplectic glass. Jaret et al. (2014) suggested that these twin features occur at relatively low shock levels where energies are low enough to be disrupted by orientation effects. At higher shock levels, energies are great enough to overcome orientation barriers.

At moderate and high shock, feldspars are transformed to diaplectic glass, an amorphous material that retains the grain boundaries of the original crystalline feldspar. Amorphization of feldspar in impacts has been subject to significant study and debate since the 1960’s (Arndt et al., 1982; Bunch et al., 1967; Chen and El Goresy, 2000; Diemann and Arndt, 1984; Fritz et al., 2005; Gillet and Goresy, 2013; Jaret et al., 2015; Kieffer et al., 1976; Milton and Decarli, 1963; Stöffler, 1971). Presently, there is still not consensus as to the specific mechanisms or impact-related amorphization of feldspars.
5.3.1 Previous Raman Studies

Raman spectroscopy probes inelastic scattering of monochromatic light and is sensitive to low-frequency lattice mode vibrations and is therefore useful for characterizing crystal structure. The frequency and number of vibrations depend on the crystal lattice and composition, which allows for unique identification of minerals. Raman lines appear as narrow peaks, shifted in energy relative to the input excitation laser frequency. Raman has been widely applied to shocked materials for both identification of high-pressure, high-temperature polymorphs and to characterize deformation level within shocked feldspars (Fritz et al., 2005; Jaret et al., 2015; Velde et al., 1989). Micro-Raman analyses of naturally shocked microcline from the Lake Mistastin impact structure (Velde and Boyer, 1985) showed a loss of diagnostic peaks at 1052 and 994 Δcm\(^{-1}\) and widening of peaks at 1115 and 474 Δcm\(^{-1}\). Similar broadening of the 1115 Δcm\(^{-1}\) peak was also seen in shocked K-feldspar from the Tenoumer impact crater, Mauritania (Jaret et al., 2014). Velde et al. (1989) analyzed Raman spectra of three different feldspar compositions experimentally shocked from 21 to 54 GPa. Anorthite showed decreasing Raman intensities up to around 30 GPa. Above 30 GPa, the sample was amorphous, as indicated by the convergence of peaks at 460 and 506 Δcm\(^{-1}\). Albite, however, retained crystallinity to 50 GPa, as seen by the presence of a sharp peak at 580 Δcm\(^{-1}\). Analysis of both experimentally shocked albite and anorthite showed that the crystalline-to-amorphous is transition was gradual, with a pressure region where the sample was a mixture of crystalline and amorphous material. Heymann and Hörz (1990) acquired Raman spectra of oligoclase (An\(_{19}\)) and andesine (An\(_{49}\)) experimentally shocked at pressures from 24 to 40 GPa. They noted the broadening and/or loss of many spectral lines with increasing pressure, culminating in the disappearance of the Si-O-Al stretch bands at >30 GPa (where the transition to diaplectic glass nears completion).

5.3.2 Previous IR studies

Infrared spectroscopy is used for analyzing molecular structure and linkages between TO\(_4\) tetrahedra (where T = either Al or Si in silicates). For feldspars, peaks between 950 and 1150 cm\(^{-1}\) correspond to Si-O stretching modes of the SiO\(_4\) tetrahedra. Peaks between 700 and 850 cm\(^{-1}\) correspond to Si-bridging oxygen modes, and peaks between 400 and 600 cm\(^{-1}\) correspond to O-
Si-O bending modes (Iiishi et al., 1971; Okuno, 2003). The specific position of the peak for each category is also dependent on specific feldspar composition (e.g., the varying Si and Al polymerization), orientation, local chemical environment, and/or substitutions or impurities.

Ostertag (1983), conducted transmission IR analyses of sanidine, orthoclase, microcline, plagioclase, and labradorite from oriented single-crystal shock experiments, shocked between 10.5 and 45 GPa. He showed that increased shock level corresponds to a general weakening of absorption bands, particularly the Si-Si and O-T-O bands. Additionally, he noted that the Si-O stretching bands between 900 and 1200 cm$^{-1}$ shift slightly and decrease intensity with shock pressure. He found a progressive sequence of deformation features in response to shock and a compositional effect where calcic feldspars transform at lower shock pressures than more Na or K-rich samples. Petrographically, fracturing and planar elements were reported below 22 GPa. Mosaicism was found to occur at 14 GPa in alkali feldspars and 18 GPa in bytownite. The more calcic plagioclase samples became amorphous by 30 GPa, whereas oligoclase (An$_{10-30}$) remained crystalline up to 34 GPa and microcline until 45 GPa.

Similarly, (Stoffler, 1972; Stöffler, 1971) showed that increased shock level corresponds with degradation of the infrared spectra towards an amorphous material (diaplectic glass) which only shows broad absorption bands near 1000, 720, and 470 cm$^{-1}$. This has been shown for natural samples from Manicouagan and Lonar craters (Arndt et al., 1982; Diemann and Arndt, 1984; Jaret et al., 2015) and was interpreted to indicate that feldspar composition diaplectic glass retains some remnants of its original feldspar crystalline structure.

The samples used here have been previously studied by thermal infrared emissivity (Johnson et al., 2002, 2003; Johnson 2012). The thermal infrared bulk emissivity spectra of these experimentally shocked minerals demonstrated significant changes with increasing pressure. In unshocked bytownite strong absorption bands occurred at 1115 cm$^{-1}$ and near 940 cm$^{-1}$ and weak bands near 500-650 cm$^{-1}$. In unshocked albite spectral features were sharper and shifted to higher wavenumbers near 800-1200 cm$^{-1}$, whereas the positions of andesine spectral features were intermediate. However, shocked plagioclase feldspars exhibited a loss of spectral features associated with Si-O stretch and bending vibrations in silica tetrahedra during the pressure-induced transition to amorphous glass. At the highest shock pressures feldspars lost all but two major spectral features, a deep band near 440-460 cm$^{-1}$ (caused by bending vibrations in the Si-O-Al structures) and broad Si-O stretch bands at 960 cm$^{-1}$ (bytownite), 1015 cm$^{-1}$ (andesine), and 1035
cm\(^{-1}\) (albite). Such spectral differences among plagioclase with pressure are related to the greater resilience of albite to shock pressure (Johnson et al., 2003; Sazonova et al., 2007), possibly owing to the higher Al content (and weaker Al-O bonds) in Ca-rich plagioclase (e.g., Fritz et al., 2011). Changes in the positions and/or band depths of spectral features were well correlated with peak shock pressures, including the position of the Christiansen feature (CF). The CF position is correlated to silicate polymerization, mineral composition (Conel, 1969) and to igneous rock type (Logan et al., 1973; Salisbury and Walter, 1989). Although some workers noted that the CF position stays at the same wavelength in spectra of <50 µm plagioclase (Nash et al., 1993; Nash and Salisbury, 1991), Johnson et al. (2002) and Johnson (2012) demonstrated that the CF positions in spectra of mm-sized chips of bytownite and andesine shifted to longer wavelengths with increasing pressure.

5.4 Samples

The samples used here are from our previous work, where we acquired thermal infrared spectra (250-2000 cm\(^{-1}\)) at macroscopic (cm) scales of experimentally shocked (15-60 GPa), nearly monominerallic anorthosites dominated by bytownite (An\(_{79}\)), andesine (An\(_{36-46}\)), and albitite (An\(_{02}\)) (Johnson et al., 2002, 2003, Johnson, 2012). Samples were selected with randomly oriented, millimeter-sized crystals to minimize the possible bias of crystal-lattice orientation on the degree and type of shock deformation from the propagating shock wave. The powder propellant gun (Flat Plate Accelerator) at the Johnson Space Center was used to conduct the shock experiments, from which relatively large chips (2-10 mm; ~300 mg) were recovered.

5.5 Methods

Small fragments of the available shocked samples were made into polished thin sections, and optical petrography was conducted using a standard Olympus petrographic microscope. Micro-FTIR point spectra of locations in the thin section were collected in the Center for Planetary Exploration at Stony Brook University using a Nicolet iN10MX FTIR microscope, equipped with a deuterated triglycine sulfate (DTGS) detector, with a spectral range of 400-4000 cm\(^{-1}\) (2.5-25 µm). We chose a spot size of 40 x 40 µm for these analyses, with spectral sampling of 8 cm\(^{-1}\). Micro-FTIR hyperspectral maps of thin sections were acquired using the same instrument equipped with a 16 pixel liquid nitrogen-cooled HgCdTe linear array detector capable of acquiring
hyperspectral image cubes between 7000 and 715 cm\(^{-1}\) (1.4-14.0 µm) at 25 µm/pixel and 8 cm\(^{-1}\) spectral sampling. Spectra were normalized to 100% maximum reflectance for ease of comparison.

Micro-Raman spectra were acquired using a WiTec alpha300R confocal imaging system equipped with 532 nm Nd YAG laser with 2.24 mW nominal power at the sample surface, and a 50X (NA=0.8) objective (spot size of 763 nm). Each analysis consisted of 240 1-second integrations that were averaged. For Raman and micro-FTIR spot analyses, multiple locations were analyzed per sample.

5.6 Results

5.6.1 Petrography

Plane- and cross-polarized transmitted light photomicrographs are shown in Figures 5.1-5.3. With increasing shock there is a general progression of decreasing birefringence in cross-polarized light.

Albite samples shocked up to 38.0 GPa show increased fracturing and are darker than the unshocked sample in plane-polarized light, but show no traditional shock metamorphic textures. Albite samples shocked to 44.6 and 50.0 GPa show decreased birefringence and a patchy extinction reminiscent of “mosaicism” seen in naturally shocked feldspars. By 55.0 GPa, albite is fully optically amorphous (Figure 5.1).

Andesine samples shocked up to 34.5 GPa show minor fracturing, are darker than the unshocked sample in plane-polarized light, but show no traditional shock metamorphic textures. Patchy extinction and mosaicism is seen in andesine shocked between 35.3 and 47.5 GPa. Andesine samples shocked to 50.0 and 53.0 GPa are nearly fully isotropic, but retain some regions of weak birefringence. Andesine shocked to 55.6 GPa is fully optically isotropic (Figure 5.2).

Bytownite samples shocked up to 22.6 GPa appear largely undeformed petrographically, but are darker than the unshocked sample in plane-polarized light. Bytownite samples shocked between 25.5 and 37.5 GPa exhibit mosaicism and are highly heterogeneously shocked with multiple domains retaining their birefringence. Above 38.0 GPa, albite is fully optically amorphous (Figure 5.3).

5.6.2 Infrared Spectroscopy

Albite
Infrared spectra (from 400 to 1500 cm\(^{-1}\)) of albite shocked up to 55.8 GPa are shown in Figure 5.4. Unshocked albite exhibits peaks at 1142, 725, and 591 cm\(^{-1}\), and a doublet at 1012 cm\(^{-1}\). Multiple spots on the same sample show that the relative intensities and exact location of these peaks can vary, presumably due to orientation of the individual grains being measured. Up to 31.4 GPa, albite shows no changes to the IR spectra. At pressures between 34.8 and 44.6 GPa, slight changes are discernable, specifically, merging of the doublet near 1012 cm\(^{-1}\) for some orientations, a broadening of the 725 cm\(^{-1}\) peak, and a decrease in intensity of the broad peak near 591 cm\(^{-1}\). At 50.0 GPa, the peak near 1142 cm\(^{-1}\) has disappeared, and the peaks near 725 and 591 cm\(^{-1}\) have merged to form one broad peak with a shoulder at 700 cm\(^{-1}\). At 55.8 GPa, only a broad peak near 1000 cm\(^{-1}\) and its associated shoulder remain present, indicating a transition to an amorphous material

**Andesine**

Infrared spectra (from 400 to 1500 cm\(^{-1}\)) of andesine shocked up to 56.5 GPa are shown in Figure 5.5. Unshocked andesine exhibits peaks at 1149, 1008, 732, 595, and 690 cm\(^{-1}\). Up to 26.4 GPa, spectra do not show discernable differences from each other. However, they exhibit just one broad peak at 590 cm\(^{-1}\) compared to the unshocked sample. This peak corresponds to a O-Si(Al)-O bending vibration which is still present within the glass (Iiishi et al., 1971). At 28.4 GPa, the peaks near 1149 and 1008 cm\(^{-1}\) have merged to form a broad peak and shoulder at 1000 cm\(^{-1}\). Between 29.4 and 33.8 GPa, andesine exhibits a broad peak near 1000 cm\(^{-1}\) and a single peak at 600 cm\(^{-1}\). Above 33.8 GPa, andesine in general only exhibits one peak near 1000 cm\(^{-1}\). Within each sample, however, some grains do occasionally exhibit slight differences such as shoulders at 1100 cm\(^{-1}\). We discuss this in more detail in the discussion section.

**Bytownite**

Infrared spectra (from 400 to 1500 cm\(^{-1}\)) of bytownite shocked up to 56.3 GPa are shown in Figure 5.6. Unshocked bytownite exhibits peaks at 1123, 960, 740, 630 and 580 cm\(^{-1}\). Up to 25.5 GPa, spectra do not show discernable differences from each other. Compared to the unshocked sample, these samples have peak intensities of the 1100 cm\(^{-1}\) peak that are lower than the unshocked sample. Above 27.0 GPa, andesine in general only exhibits one peak near 1000 cm\(^{-1}\). Within each sample, however, some grains do occasionally exhibit slight differences such as
shoulders at 1100 cm\(^{-1}\). In these samples, while the spectral shape does not change, up until 56.3 GPa, the exact position of the broad peak at 1000 cm\(^{-1}\) changes slightly within each sample. For example, the green spectrum in Figure 5.6H, 27.0 GPa, has a peak position of 1000 cm\(^{-1}\), whereas the purple spectrum has a peak position of 960 cm\(^{-1}\). At 56.3 GPa, however, this peak position does not change within the sample.

5.6.3 Raman Spectroscopy

Albite

Micro-Raman spectroscopy results of albite shocked up to 55.8 GPa are shown in Figure 5.7. Samples shocked up to 50.0 GPa show characteristic feldspar peaks at 290, 478, and 507 \(\Delta cm^{-1}\). Additional peaks at 112, 251, 761 and 208 \(\Delta cm^{-1}\) are present in some samples, but these likely reflect slight structural or chemical variation in individual grains. Between 0 and 50 GPa, increasing shock corresponds to a general trend of decreasing intensity of peaks, particularly the 507 \(\Delta cm^{-1}\) peak (Figure 5.7). Additionally, up to 50 GPa there is a general trend of the peak ratio of the 507 cm\(^{-1}\) and 485 \(\Delta cm^{-1}\) peaks (507:481) approaching unity. Only the sample shocked to 55.8 GPa shows Raman spectra indicative of an amorphous material, specifically two broad peaks near 500 and 100 \(\Delta cm^{-1}\).

Andesine

Micro-Raman spectroscopy of andesine shocked up to 56.5 GPa are shown in Figure 5.8. Unshocked andesine exhibits peaks (in order of decreasing intensity) at 507, 479, 284, and 408 \(\Delta cm^{-1}\). Less intense peaks occur at 566 and 161 \(\Delta cm^{-1}\). In general, increasing shock level causes a decrease in peak intensity, starting with the low wavenumber peaks, leading towards a pattern showing just a broad peak near 500 \(\Delta cm^{-1}\). The sample at 15.8 GPa does not show discernable differences from the unshocked sample. Between 24.9 and 29.4 GPa, the samples show a decrease in overall intensity of peaks, a 507:485 peak ratio approaching unity, increased background fluorescence, and within each sample some of the individual spots have lost all crystalline peaks. Above 33.8 GPa, only a broad peak at 500 \(\Delta cm^{-1}\) remains.

Bytownite

Micro-Raman spectra of bytownite shocked up to 56.3 GPa are shown in Figure 5.9. Compared to the unshocked sample, all samples show a significant decrease in the relative intensities of characteristic peaks at 290, 478, and 507 \(\Delta cm^{-1}\). Between 17.0 and 25.5 GPa the
samples show a general decreasing trend in peak intensities and a 507:485 peak ratio approaching unity. These samples, however, are quite heterogeneous, with occasional regions showing stronger peak intensities. Between 25.5 and 38.2 GPa, samples show higher fluorescence, a loss of peaks below 300 Δcm⁻¹, and one broad peak centered near 500 Δcm⁻¹. Like the samples shocked at lower peak pressures, these are heterogeneously shocked and show regions that have retained some crystallinity, as shown by the two discernable peaks at 485 and 507 Δcm⁻¹ present in some locations. Above 38.2 GPa, the samples exhibit only broad peaks near 500 and 1000 Δcm⁻¹, and are relatively homogenous, without regions that retained any crystallinity.

5.7 Discussion

Petrographically, all three compositions show a general trend of disordering with increased shock, specifically a decrease in birefringence. Interestingly, however, no traditional shock metamorphic microstructures are seen in any samples. There is an increase in fracturing and cracking of grains, but this texture is not uniquely indicative of shock, and in naturally shocked samples this would not be a sufficient indicator of shock metamorphism (French and Koeberl, 2010). One sample, bytownite shocked to 22.6 GPa, shows microfaulted, offset and slightly rotated twins (Figure 5.10A). This texture is not considered diagnostic of a shock wave (French and Koeberl, 2010) but does occur readily in natural impactites, such as reported at Lapparjarvi (Reimold, 1982) or at the Gardnos impact structure (Figure 5.10B). In the experimentally shocked bytownite, the offset twins are clearly associated with the impact deformation. Constraining the localized pressure and strain-rate conditions that formed this texture could aid our understanding of how and at what stage in the cratering process these offset twins form in natural impacts.

PDFs, which are known to occur in naturally shocked quartz and feldspar (Bischoff and Stöffler, 1984; Jaret et al., 2014; Pati et al., 2010; Reimold, 1982) and which occur readily in experimentally shocked quartz (Grieve et al., 1996; Huffman and Reimold, 1996) are not seen in any of these samples. These samples cover the range of pressures over which PDFs form in experimentally shocked quartz, and IR and Raman analyses of these samples do show they have been disordered structurally, yet optical PDFs have not been produced. Additional characterization work at micro- and nano-scales is necessary to fully understand how the disordering is manifested at these scales.
The most prominent petrographic texture seen in thin section from all samples here is an apparent darkening associated with increased shock. As seen under plane-polarized light, with increasing shock level, samples become progressively more opaque. Darkening associated with shock has been reported before, primarily in olivines in meteorites. Shock darkening in meteorites is somewhat controversial, and often suggested to have to do with finely disseminated sulfides and Fe-metals or due to frictional melting (Bischoff et al., 2006; Britt and Pieters, 1994). Shock-darkening in tectosilicates has been reported in natural terrestrial impactities, such as the “black quartzite” at the Gardnos, Manson, and Roter Kamm impact structures (French et al., 1997; Koeberl et al., 1996; Reimold and Miller, 1989). The specific structure and mechanism of this darkening is still largely unknown but it has been suggested to be an optical effect due to a dramatic increase of dislocations at the atomic level. One possibility is that the darkening seen here is contamination from the sample container, but this seems unlikely as it is a pervasive feature throughout the sample. This darkening was seen on the mm-sized recovered chips and was seen at all thicknesses during the thin sectioning process. If it is contamination, then some additional process is operating to allow for container material to interact throughout the entire volume of the sample.

5.7.1 Amorphization Pressures

Based on our spectroscopic analyses, we place an amorphization point between 25.5 and 27.0 GPa for bytownite, between 28.4 and 29.4 GPa for andesine, and between 50 and 55.8 GPa for albite. This is slightly lower than where the thin sections suggest the samples are fully optically isotropic (Figure 5.1). This discrepancy is likely due to difficulties interpreting the thin sections given the significant heterogeneity across the thin section, and the difference in spatial scale between thin sections and micro-spectroscopy. Our spectroscopy results are consistent with pervious experimental studies conducted at different shock facilities (Huffman and Reimold, 1996; Okuno et al., 1985; Ostertag, 1983; Velde et al., 1989).

Both the IR and the Raman spectroscopy place the amorphization point at the same shock level, but at a lower shock level than estimated by petrography. This is consistent with previous (Jaret et al., 2014; Williams, 1998) that suggested spectroscopy may be more sensitive to internal deformation than optics alone.
Interestingly, the IR spectra show multiple transitions rather than a single amorphization point. While the samples above the amorphization point have amorphous spectral shapes, the specific position of the large broad peak changes. Such change in peak position has been interpreted by Jaret et al. (2015) as indicative of remnant orientation. For example, the bytownite samples shocked to 29.3, 37.5, and 38.2 GPa show peak positions that vary across the sample by up to 40 cm$^{-1}$ (Figure 5.6). At 49.2 and 56.3 GPa, however, that variation in peak position is not seen, suggesting there may be another transition where at the highest pressures bytownite no longer exhibits any remnant orientation.

Across all techniques, shocked samples display significant heterogeneity. As illustrated in Figures 5.1-5.3 within each sample, particularly for the lower shocked samples, some areas remain crystalline while adjacent grains or sub-grain domains have become amorphous. The micro-scale heterogeneity seen here is similar to what is observed in naturally shocked impactites. There are several possible explanations for the observed micro-scale heterogeneity. First, this could be due to heterogeneity within the shock wave itself (Fritz et al., 2017 and references therein). Secondly, this could be due to refractions and impedances as the shockwave crosses between grains, especially for adjacent grains of different composition. The bytownite sample is not pure, with accessory pyroxenes and amphiboles. Lastly, the heterogeneity in shock response could be due to orientation effects of the individual grains. Shock response is known to be orientation-sensitive where grains oriented parallel to the shockwave tend to show more evidence of shock. This has been suggested as an explanation for why naturally shocked quartzites often show PDFs in some grains but not in neighboring grains. Orientation effects could also explain why shock heterogeneity was not observed by (Johnson, 2012; Johnson et al., 2003, 2002) despite measuring the same samples. Previous studies used large spot sizes and IR techniques that were either on powders or averaged large areas of the sample, thus not allowing documentation of any orientation effects. Jaret et al., 2014 suggested that shock heterogeneity plays a more important role in lower shock regimes, and that at the highest shock levels there is sufficient energy to overwhelm minor impedences due to orientation. Similarly in this study, total energy imparted could explain our observation that the highest shocked bytownite samples are relatively homogeneous compared to the other samples.

The heterogeneity at the small spatial scale seen here complicates efforts to use spectroscopy as a quantitative measure to determine shock level within samples. For example, a
plot of Raman peak intensity of the primary $507 \Delta \text{cm}^{-1}$ peak in albite vs. pressure (Figure 5.11) shows a general decrease in intensity with pressure but there is enough scatter within each sample that it is not a unique indicator of shock level. It is possible to distinguish samples shocked to 55 GPa can be distinguished from unshocked samples, but the range of peak intensities overlap with the adjacent pressures. Likewise plots of the ratio of the two primary Raman peaks for albite ($479/508 \Delta \text{cm}^{-1}$) shows a general trend, but again, the scatter within each sample does not allow for this to be a unambiguous measure of shock level (Figure 5.12). This is also the case for the andesine and bytownite.

As seen in the infrared spectra, we do not see a correlation between CF position and shock level (Figure 5.13), nor is there a correlation between band depth at $1007 \text{ cm}^{-1}$ and shock pressure (Figure 5.14). Like the Raman peak ratios (Figure 5.11) the band depth qualitatively decreases with shock pressure, but there is enough variability within the samples that this parameter cannot be considered unique to any given shock state.

5.8 Conclusions

Petrographically, these experimentally shocked feldspars appear to show slightly different textures than naturally shocked samples. Up to ~50 GPa, none of the bytownite, andesine, or albite samples display traditional shock microstructures (i.e., PDFs). However, micro-Raman and micro-FTIR spectra indicate these samples are undergoing the expected trends in internal disordering. Additionally, these samples show a pronounced darkening in plane-polarized light. Such darkening has been reported in naturally shocked meteorites and terrestrial samples, although only rarely, and has not been the subject of detailed spectroscopic or crystallographic study.

In these samples, shock effects are heterogeneously distributed within the sample. As a result, micro-spectroscopy does not provide unique indicators of shock level. We see general trends in degradation of both the IR and Raman spectra, but it is not possible to assign spectral characteristics to a specific shock level.

For these samples, we interpret the amorphization pressure in experimentally shocked samples between 50.0 and 55.8 GPa for albite, between 28.4 and 29.4 GPa for andesine, and between 25.5 and 27.0 for bytownite. All techniques used (i.e., IR, Raman, and optical petrography) place the amorphization point at the same shock level despite the heterogeneity addressed above. These values are consistent with previous experiments, albeit under different
experimental setups, and the progression of higher amorphization pressure for more sodic feldspars is also consistent with previous work (Huffman and Reimold, 1996; Okuno, 2003; Ostertag, 1983). Importantly, these values represent amorphization in these experiments that do not have the same strain rates or temperatures associated with natural impacts. Therefore, it may not be straightforward to assume natural samples will become amorphous at this same pressure regime.

5.9 References


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Figure 5.1: Plane- and cross-polarized light images of experimentally shocked albite.
Figure 5.2: Plane- and cross-polarized light images of experimentally shocked andesine
Figure 5.3: Plane- and cross-polarized light images of experimentally shocked bytownite.
Figure 5.4: Infrared spectra (1500 to 400 cm\(^{-1}\)) of shocked albite acquired with the DTGS detector. Generally, there is a decrease in overall intensity with shock level, and above at 55.8 GPa and above, the sample is amorphous.
Figure 5.5: Infrared spectra (1500 to 400 cm$^{-1}$) of shocked andesine acquired with the DTGS detector. Generally, there is a decrease in overall intensity with shock level. The transition to fully amorphous material is between 29.4 and 33.8 cm$^{-1}$. 
Figure 5.6: Infrared spectra (1500 to 400 cm\(^{-1}\)) of shocked bytownite acquired with the DTGS detector. Generally, there is a decrease in overall intensity with shock level, but the samples are quite heterogeneous on an individual grain basis. The transformation to amorphous material occurs at 27.0 GPa.
Figure 5.7: micro-Raman spectra of albite samples. Spectra have had cosmic rays removed, but have not been baseline corrected.
Figure 5.8: micro-Raman spectra of andesine samples. Spectra have had cosmic rays removed, but have not been baseline corrected.
Figure 5.9: micro-Raman spectra of albite samples. Spectra have had cosmic rays removed, but have not been baseline corrected.
Figure 5.10: Offset twins in response to impact deformation. A) Bytownite shocked to 22.6 GPa. B) naturally shocked feldspar from the Gardnos Impact Structure, Norway.
Figure 5.11: Raman peak intensities of the $\Delta 507\text{cm}^{-1}$ peak in shocked albite, showing a general decrease in intensity with shock pressure.
Figure 5.12: Raman peak ratios of the 479 and 508 Δcm⁻¹ peaks in albite. There is a general trend of higher ratio with increasing shock level, particularly the highest shock level, but there is significant scatter within each sample set so this is not a diagnostic indicator of shock level.
Figure 5.13: CF position variation with pressure for andesine samples. We do not see a correlation between CF position and shock pressure.
Figure 5.14: Infrared band depths of the 1007 cm$^{-1}$ peak in andesine samples.
Chapter 6
Conclusions

In this dissertation, I focused on the mineralogical and geochemical changes in silicates in response to impact cratering. These results are important for future studies of extraterrestrial planetary bodies – both remote and returned samples – because we will inevitably encounter shocked material. Therefore, understanding how impacts change silicate structures and geochemistry is critical for correct interpretations. In many cases, the goal of such studies is to understand the formation of these other planets, but they have been overprinted by impact cratering. So, we must be able to recognize (and separate if we can) features related to the secondary impact process from those reflecting the primary geology.

Each chapter contains its own set of conclusions, but here I summarize some major finding and discuss new questions relevant to this work. In Chapter 1, the major conclusion is that we are able to distinguish solid-state glass from fused glass, because solid-state glass is anisotropic in the infrared. Anisotropic glasses are interesting from a structural chemistry standpoint but have not been heavily studied. A likely follow-up of this chapter would be a detailed (using Transmission Electron Microscopy) characterization of these glasses at an atomic scale. Feldspars, however, are complex chemically, and so it may be useful to look at the SiO$_2$ system instead. If diaplectic quartz is also anisotropic, it may be easier to understand formation mechanisms in that simpler system. Or, is there something about the feldspar structure that allows for anisotropy? Lastly, although this chapter made progress in recognizing and characterizing shock-amorphous feldspars, I did not thoroughly discuss formation mechanisms. Another follow-up study would be to examine the proposed mechanism for producing dialectic glass in more detail, again ideally at the atomic level.

Chapter 2 focused on the formation of coesite at the Lonar crater. Here I showed for the first time, presence of coesite at Lonar. Importantly, this phase occurs only within shocked amygdules and is likely due to extremely localized increases in temperature due to collapsing vesicle walls. This work has potential for application to meteorites, where high-pressure, high-temperature phases occur along cracks and fractures due to similar collapse of void space. My work here suggests that vesicles could be another morphology in which to search for high pressure phases in meteorites. The other conclusion of this chapter is that pre-impact target properties dictate what happens during shock. In the case of Lonar, the target was altered (i.e., silica precipitated in the vesicles). This serves as a cautionary tale for studies of other terrestrial impact
structures that the rheology and mineralogy of the rocks at the time of impact are critical, particularly for attempts to model impacts.

Chapter 3 focused on $^{40}$Ar/$^{39}$Ar analyses of maskelynite from the Manicouagan impact structure. I show that the maskelynite is partially reset, and yields an age that is in between the target and impact age. Furthermore, the degassing pattern from step-heating experiments is not similar to that of thermal metamorphic events. This important finding shows that unlike in shock experiments, natural impacts can affect the argon isotopic system and thus argon ages for lunar and martian maskelynite may not provide geologically relevant ages. One likely follow-up to this study is to consider the effects of grain size. The sample used here is a coarse grained anorthosite which is analogous to the Moon but significantly coarser than martian maskelynite, which is basaltic. Diffusion is grain size dependent, and so now that partially reset large grains has been documented, could smaller grains be more fully (or completely) reset? One empirical test would be to look at naturally shocked basalts from Lonar. I would like to note that $^{40}$Ar/$^{39}$Ar dating of maskelynite from Lonar was originally one of my proposed projects, but the Lonar samples are small and have low K abundances, thus being analytically difficult. However, more contemporary mass spectrometers may be able to measure such low concentrations.

Chapter 4 focused on characterizing experimentally shocked plagioclase using optical petrography, micro-Raman and micro-FTIR spectroscopy. The major discovery of this project are recognizing the importance of shock heterogeneity on a micro-scale, and identifying some unexpected differences between experimentally and naturally shocked feldspars. Specifically, none of the experimentally shocked samples show traditional textures unique and indicative of shock (e.g. planar deformation features). One sample shows offset twins, which are common in naturally shocked samples, but are likely by sub-shock shear conditions. However, all samples show spectroscopic evidence of internal deformation in response to shock. An initial review of literature on experimentally shocked feldspars has failed to find examples of PDFs in feldspars produced experimentally; one interpretation of this is that perhaps PDF formation in feldspars is more complicated than in quartz. The difference feldspar response between natural and experimental shocked plagioclase has not been recognized previously and is the subject of some of my ongoing work. Understanding how these samples have changed at an atomic level would be necessary to explain why they appear deformed spectroscopically yet lack traditional textures.
The overarching themes from this work are i) the role of heterogeneity in impact metamorphism and ii) separating impact deformation that involved melting from that which is purely solid-state. Impact events are heterogeneous. While this has been known for decades, I was still surprised at the scale of heterogeneity. In the shocked basalts from Lonar, we see extremely localized areas of melting within bulk samples that were demonstrably deformed purely by solid-state processes. In the experimentally shocked samples, I have shown variation in deformation level across 1-2 mm samples. In some cases, crystalline grains were immediately adjacent to amorphous grains. This complexity at the micro-scale raises questions and highlights challenges of interpreting “bulk” or “average” shock conditions.

As shown in Chapters 1, 2 and 3, impact melt products are fundamentally different from those that deformed via solid state. The maskelynite from the Lonar crater can be distinguished from melt-glass by preservation of remnant orientation effects in the IR spectra suggesting the grains have become amorphous but have not been fully atomically homogenized. Similarly, SiO$_2$ glass can be separated into multiple amorphous phases using NMR spectroscopy as shown in Chapter 2. And in terms of geochronology, as shown in Chapter 3, impact melt samples behave completely differently than maskelynite. The innovation of this study was combining spectroscopy and geochemistry in order to distinguish melt from non-melt and target selected grains. It will be useful to apply this approach to more complicated rocks such as impact melt-breccias (or lunar breccias). Ultimately, the take-home message is that shocked samples are complex and benefit from a multi-technique approach. As I have shown petrography, infrared spectroscopy, X-Ray spectroscopy, NMR spectroscopy, and Raman spectroscopy each has different capabilities it is possible to misinterpret formation conditions or mechanisms if only using any one technique.