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Key Points:

- More anorthitic plagioclase is less resistant to shock pressures
- At small spatial scales, shock effects are heterogeneous

Supporting Information:

- Supporting Information S1

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Microspectroscopic and Petrographic Comparison of Experimentally Shocked Albite, Andesine, and Bytownite

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Abstract Plagioclase feldspars are common on the surfaces of planetary objects in the solar system such as the Moon and Mars, and in meteorites. Understanding their response to shock deformation is important for interpretations of data from remote sensing, returned samples, and naturally shocked samples from impact craters. We used optical petrography, micro-Raman, and micro-Fourier transform infrared spectroscopy to systematically document vibrational spectral differences related to structural changes in experimentally shocked (0–56 GPa) albite-, andesine-, and bytownite-rich rocks as a function of pressure and composition. Across all techniques, the specific composition of feldspars was confirmed to affect shock deformation, where more Ca-rich feldspars transform to an amorphous phase at lower shock conditions than more Na-rich feldspars. Onset of amorphization occurs at ~50 GPa for albite, between 28 and 30 GPa for andesine, and between 25 and 27 GPa for bytownite. Complete amorphization occurred at pressures greater than ~55 GPa for albite, ~47 GPa for andesine, and ~38 GPa for bytownite. Petrographically, these experimentally shocked samples do not exhibit the planar microstructures common in naturally shocked plagioclase, despite showing the expected trends of internal disordering and deformation as seen in the micro-Raman and infrared spectra. Average spectra of hyperspectral images of these samples mimic macroscale measurements acquired previously. However, we see micro-scale heterogeneity in the shock response, resulting from variations in either composition, crystal orientation, or the inherent heterogeneity of the shock wave topology. This is an important factor to consider when deducing shock pressures in naturally shocked samples.

Plain Language Summary We have analyzed experimentally shocked plagioclase-bearing rock samples with a variety of small spatial scale spectroscopic techniques. The pressures at which these samples become a glass are consistent with previous shock and static compression experiments. We have confirmed a compositional effect on shock deformation, where more-Ca rich phases become glass at lower pressures. However, we find significant heterogeneity, most likely due to orientation differences among individual grains within these rocks. Understanding shock effects in rocks (opposed to single crystal experiments) will be particularly important for upcoming and future planetary missions, which will explore potentially shocked rocks with remote infrared and/or Raman spectroscopy.

1. Introduction

Impact cratering is a ubiquitous geological process 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 in rocks and minerals (French, 1998; Melosh, 1989). Collectively referred to as impact metamorphism (or shock metamorphism when referring specifically to the deformation related to the shock wave i.e., not involving melting), this process results in brecciation, melting, formation of high-pressure, high-temperature polymorphs, and other mineral-scale crystallographic deformation. 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 & Stöffler, 1992; Langenhorst, 1994; Sharp & 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 & 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 vibrational features with pressure that are associated with progressive amorphization, particularly in experimentally shocked plagioclase feldspars (Fritz et al., 2005; Heymann & 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. By analyzing the microscopic (tens of μm) 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 illustrate how shock metamorphism alters individual mineral grains in the context of their surroundings. Shock experiments with known pressure conditions are useful in understanding the spectral variations observed in naturally shocked samples, despite key differences between natural and experimental shock. For example, natural shock pulses are about 10^3 times longer in duration than in laboratory experiments (Fritz et al., 2017). Additionally, 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 (with a spot size of less than 100 μm). Using spectroscopy to address shock state in 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 parent bodies. Another application of planetary spectroscopy is in the robotic exploration of Mars. For example, the Curiosity rover on Mars has documented substantial 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-generated amorphous material can be distinguished from amorphous material formed by other processes (and if so, which tool best identifies them) would be useful to future missions or studies of returned samples. For example, the Mars 2020 rover will include two Raman instruments. The Raman component of Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals (SHERLOC) will use a 248.6 nm laser beam focused to 50 μm to map over an $\sim 7 \times 7$ mm area of selected samples, with a spectral range from 810 to $\sim 3,000$ cm^{-1} (Beegle et al., 2015). The Raman spectrometer on the SuperCam instrument will use a 532 nm laser at ~ 0.8 mrad spatial resolution (2.4 mm spot size at 3 m distance) to acquire data from ~ 150 to $\sim 4,000$ cm^{-1} (Perez et al., 2017; Wiens et al., 2017). Additionally, there will be a RLS Raman spectrometer on the future European ExoMars2020 rover (Rull et al., 2017). The work presented here will provide valuable baselines from which to interpret potential shock effects in rocks at the landing site using data from both of these instruments.

2. 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 & Reimold, 1996; Jaret et al., 2015; Stöffler, 1971; von Engelhardt & Stöffler, 1968). While the work presented here 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 and Osinski (2013), Grieve et al. (1996), and von Engelhardt and Stöffler (1968).

The optical petrographic effects of shock in feldspars are progressive (Jaret et al., 2014; Kieffer et al., 1976; Pickersgill et al., 2015; Stöffler, 1971): the appearance of PDFs, the formation of diaplectic glass, and finally, whole-scale melting. Based on the trend of shock textures in quartz, several classification schemes for assessing shock level in natural samples were developed (Chao, 1968; Singleton et al., 2011; Stöffler, 1971; von Engelhardt & Stöffler, 1968). Pressures of formation have been estimated for the transition to amorphous material and are typically calibrated based on shock experiments (Horz & Quaide, 1973; Huffman et al., 1993; Ostertag, 1983; Stöffler, 1971; von Engelhardt & Stöffler, 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 (Jaret et al., 2014; White, 1993). 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. Impact-induced amorphization of feldspars has been subject to significant study and debate since the 1960s (Arndt et al., 1982; Bunch et al., 1967; Chen & El Goresy, 2000; Diemann & Arndt, 1984; Fritz et al., 2005; Gillet & El Goresy, 2013; Jaret et al., 2015; Kieffer et al., 1976; Milton & Decarli, 1963; Stöffler, 1971). Feldspars can deform under solid-state mechanisms (Arndt et al., 1982; Diemann & Arndt, 1984; Horz & Quaide, 1973; Jaret et al., 2015) or by quenching from a melt (Chen & El Goresy, 2000; Ferrière & Brandstätter, 2015; Gillet & El Goresy, 2013). Unfortunately, the term “maskelynite” has been used in the literature to describe both melt-glass and diaplectic glass. To avoid further confusion, in this paper, refrain from using the term maskelynite, and instead describe our samples as diaplectic glass.

2.1. Previous Raman Studies

Raman spectroscopy probes inelastic scattering of monochromatic light and is sensitive to low-frequency lattice mode vibrations 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 spectroscopy 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).

Freeman et al. (2008) used calculations from McKeown (2005) to designate five groups of Raman spectral peaks associated with plagioclase. Group I includes the $450\text{--}520\text{ cm}^{-1}$ spectral region related to the stretching motion of the TO_4 tetrahedra (where T = either Al or Si in silicates). Groups II ($\sim 240\text{--}300\text{ cm}^{-1}$) and III ($\sim 150\text{--}210\text{ cm}^{-1}$) correspond to rotation-translation modes (also referred to as lattice modes by Sharma et al., 1983), Group IV ($\sim 550\text{--}830\text{ cm}^{-1}$) includes deformation modes, and Group V ($\sim 875\text{--}1,200\text{ cm}^{-1}$) comprises vibrational stretching modes of the tetrahedra. Sharma et al. (1983) further subdivided these into asymmetric Si-O-Al stretching vibrations ($908\text{--}990\text{ cm}^{-1}$) and Si-O-Si vibrations ($1,044\text{--}1,124\text{ cm}^{-1}$).

Micro-Raman analyses of naturally shocked microcline from the Lake Mistastin impact structure (Velde & Boyer, 1985) showed a loss of diagnostic peaks at $1,052$ and 994 cm^{-1} and widening of peaks at $1,115$ and 474 cm^{-1} . Similar broadening of the $1,115\text{ cm}^{-1}$ 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 cm^{-1} . Albite, however, retained crystallinity to 50 GPa, as seen by the presence of a sharp peak at 580 cm^{-1} . Analysis of both experimentally shocked albite and anorthite showed that the crystalline-to-amorphous transition was gradual, with a pressure region where the sample was a mixture of crystalline and amorphous material. Heymann and Horz (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).

2.2. Previous Infrared Studies

Infrared spectroscopy is used for analyzing molecular structure and linkages between TO_4 tetrahedra. For feldspars, reflectance peaks between 950 and $1,150\text{ cm}^{-1}$ (reststrahlen bands) 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. As such, precise chemical compositional information is required for correctly interpreting the degree of deformation from an infrared spectrum.

Ostertag (1983) conducted transmission infrared 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 1,200 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, Stöffler (1971, 1972) showed that increased shock level corresponds with degradation of the infrared spectra toward an amorphous material (diaplectic glass), which only shows broad absorption bands near 1,000, 720, and 470 cm^{-1} . This has been shown for natural samples from Manicouagan and Lonar craters (Arndt et al., 1982; Diemann & Arndt, 1984; Jaret et al., 2015), and remnant infrared spectroscopic anisotropy in the diaplectic plagioclase glass was interpreted to indicate that shocked diaplectic glass retains some remnants of its original feldspar crystalline structure (Jaret et al., 2015).

The samples investigated here were previously studied using macroscopic (cm) scale thermal infrared reflectance and emissivity (Johnson, 2012; Johnson et al., 2002, 2003) and demonstrated significant spectral changes with increasing pressure. Overall changes with pressure result from the distortion of stronger, tetrahedral (four-fold) Si-Al coordination bonds to weaker, less polymerized bonds associated with octahedral (sixfold) coordination (e.g., Fritz et al., 2005; Johnson et al., 2002). In unshocked bytownite, strong emission minima (reflectance peaks) occurred at 1,115 cm^{-1} and near 940 cm^{-1} and weak bands near 500–650 cm^{-1} . In unshocked albite, spectral features were sharper and the main band shifted to higher wavenumbers (1,140 and $\sim 1,020 \text{ cm}^{-1}$), whereas the positions of andesine spectral features occurred at $\sim 1,130$ and $\sim 1,000 \text{ cm}^{-1}$. Shocked samples exhibited a loss of spectral features associated with Si-O stretch and bending vibrations in silica tetrahedra during the pressure-induced transition to amorphous material. 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), 1,015 cm^{-1} (andesine), and 1,035 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).

Previous Fourier transform infrared (FTIR) spectroscopy measurements of the chips were used by Johnson (2006) and by Rogers and Christensen (2007) to search for shocked plagioclase in Thermal Emission Spectrometer (TES) data and by Rogers and Aharonson (2008) in their analyses of mini-TES data. We have not included discussion of those previous analyses in this manuscript owing to the large-scale nature of those observations (kilometers down to centimeters). As discussed later in this manuscript, the effect of crystal orientations at microscales complicates direct application to macroscale observations and models.

3. Samples

In total, 41 thin sections were examined for this study. The samples used here were previously experimentally shocked to pressures between 15 and 56 GPa (see Johnson et al., 2002, 2003, and Johnson, 2012, for experimental details). The starting materials consisted of monomineralic rocks with zero porosity dominated by bytownite (An_{77}), andesine (An_{43}), and albitite (An_{02}). These were then cored and sliced producing flat polished sections for shock experiments. For each composition, sections 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 starting sample for each pressure step was taken from the same rock core. The powder propellant gun (Flat Plate Accelerator) at the Johnson Space Center (Houston, TX) was used to conduct the shock experiments, from which relatively large chips

Table 1
Shock Recovery Experiment Samples

Albite ID	GPa	Andesine ID	GPa	Bytownite ID	GPa
3315	17	3510	15.8	3156	17
3313	24	3509	24.9	3154	21
3311	25.5	3508	26.4	3151	21.5
3322	27.8	3507	28.4	3155	22.6
3312	29	3513	29.4	3146	25.5
3314	31.4	3511	29.6	3145	27
3319	34.8	3514	30.6	3142	29.3
3318	38	3515	33.8	3148	37.5
3320	44.6	3512	34.5	3143	38.2
3316	50	3677	35.3	3149	49.2
3317	55.8	3516	37.6	3144	56.3
		3518	47.5		
		3519	50		
		3520	53		
		3521	56.5		

Note. Sample identification numbers refer to the Running Flat Plate Accelerator experiment number from the Experimental Impact Laboratory at Johnson Space Center (cf. Johnson, 2012; Johnson et al., 2002, 2003).

(2–10 mm; ~300 mg) were recovered. Table 1 lists the sample numbers and experimental shock pressures for the three plagioclase suites. Representative microprobe analyses of splits of the unshocked samples confirmed plagioclase compositions of An₇₇ (bytownite), An₄₃ (andesine), and An₀₂ (albite; Table 2).

4. 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 spectra were collected in the Center for Planetary Exploration at Stony Brook University using a Nicolet iN10MX FTIR microscope. Micro-FTIR hyperspectral maps of thin sections were acquired using a liquid nitrogen-cooled HgCdTe (MCT) detector, generating hyperspectral image cubes between 7,000 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. Point spectra were acquired with a deuterated triglycine sulfate (DTGS) detector, with a spectral range of 400–4,000 cm⁻¹ (2.5–25 μm). For these analyses, we chose a spot size of 100 × 100 μm representing a single spot within the grain, with spec-

tral sampling of 8 cm⁻¹. Each spectrum represented accumulations of 1,024 scans. For both point spectra and hyperspectral maps, backgrounds were collected on gold mirrors prior to measuring the sample. Background analyses used the same spot size and acquisition times as samples.

Micro-Raman spectra were acquired using a WiTec alpha300R confocal imaging system equipped with 532 nm neodymium: yttrium/aluminum/garnet (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 one-second integrations that were averaged. For Raman and micro-FTIR spot analyses, multiple locations were analyzed per sample, as discussed below.

Chemical analyses of the plagioclase samples were performed using an electron microprobe housed in the Department of Earth and Planetary Sciences at the American Museum of Natural History. Samples were mounted in epoxy, polished and carbon-coated before being loaded into a Cameca SX-100 electron microprobe. An accelerating voltage of 15 keV, and beam current of 20 nA were employed for the analyses, which

Table 2
Major Element Chemical Analyses of Plagioclase Samples

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Cr ₂ O ₃	Total	An
Albite	68.00	0.00	22.31	0.04	0.00	0.01	0.54	11.12	0.12	0.00	0.00	102.12	
Albite	66.72	0.04	21.96	0.02	0.00	0.00	0.49	10.06	0.12	0.00	0.02	99.43	
Albite	65.47	0.02	22.59	0.02	0.01	0.00	0.41	10.75	0.11	0.02	0.00	99.39	
Albite	67.66	0.01	21.72	0.03	0.01	0.00	0.41	10.34	0.12	0.02	0.01	100.33	
	66.96	0.02	22.14	0.03	0.00	0.00	0.46	10.57	0.12	0.01	0.01	100.32	2.5
Andesine	58.14	0.02	27.18	0.15	0.00	0.00	8.36	6.54	0.30	0.12	0.01	100.83	
Andesine	58.13	0.01	27.30	0.18	0.00	0.00	8.45	6.55	0.27	0.11	0.00	100.99	
Andesine	57.80	0.00	27.20	0.11	0.04	0.01	8.07	6.72	0.24	0.14	0.00	100.31	
Andesine	56.67	0.01	28.09	0.05	0.00	0.01	8.87	6.60	0.18	0.14	0.00	100.61	
Andesine	57.43	0.03	27.50	0.16	0.02	0.00	8.37	6.53	0.33	0.16	0.02	100.55	
	57.63	0.02	27.45	0.13	0.01	0.00	8.42	6.59	0.26	0.13	0.01	100.66	42.8
Bytownite	47.32	0.01	33.21	0.47	0.02	0.02	15.46	2.84	0.09	0.18	0.00	99.62	
Bytownite	48.67	0.09	32.47	0.43	0.00	0.03	15.43	2.66	0.08	0.19	0.01	100.05	
Bytownite	48.72	0.03	32.20	0.44	0.02	0.03	14.93	2.96	0.09	0.19	0.03	99.65	
Bytownite	50.37	0.03	31.00	0.36	0.02	0.02	13.70	2.79	0.11	0.18	0.00	98.57	
Bytownite	47.69	0.00	32.09	0.50	0.01	0.03	15.61	2.67	0.09	0.18	0.01	98.89	
	48.55	0.03	32.19	0.44	0.02	0.03	15.03	2.78	0.09	0.19	0.01	99.36	76.7

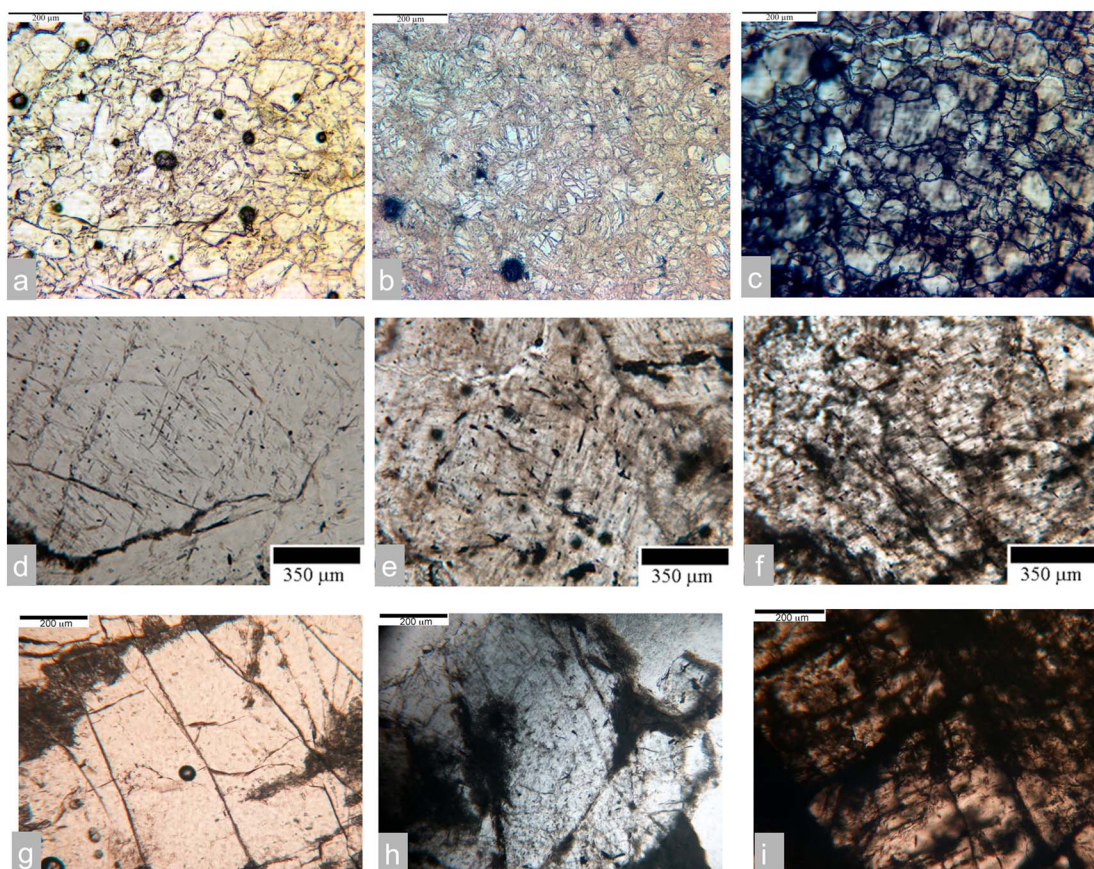


Figure 1. Plane-polarized photomicrographs of (top row) albite, (middle row) andesine, and (bottom row) bytownite at different shock pressures. (a) Unshocked, (b) 27.8 GPa, (c) 55.8 GPa, (d) unshocked, (e) 28.4 GPa, (f) 56.5 GPa, (g) unshocked, (h) 27.0 GPa, and (i) 56.3 GPa.

were all 30-s duration, using a 5- μ m diameter electron beam. Na was measured first to minimize loss over long beam exposures. Standards used for Ca and Al were Miyake-Jima anorthite, Na on McKee Jadeite, Si on Lake County Plagioclase, K on orthoclase, Fe on Rockport Fayalite, and P on Wilbur apatite. Anorthite contents were calculated from the bulk compositions using the CIPW Norm program of the IgPet software package (Carr, 2002).

5. Results

The results presented below include representative examples from unshocked (0 GPa), intermediate ($\sim$ 27 GPa), and the most highly shocked samples ($\sim$ 56 GPa) for each of the three plagioclase types. Products presented here include the microphotographs, single-point spectra acquired using the DTGS detector, hyperspectral image parameters (using the MCT detector), and Raman point spectra. Supporting information included with this paper contains similar derived data products for all samples, in addition to the single-point spectra acquired using the MCT detector. All data products will be archived in the NASA Planetary Data System (PDS) and in the Stony Brook University Academic Commons (<https://commons.library.stonybrook.edu/>).

5.1. Petrography

Plane- and cross-polarized transmitted light photomicrographs are shown in Figures 1 and 2, respectively, for shock levels of 0, $\sim$ 27, and $\sim$ 56 GPa for each plagioclase. 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 PDFs. Below 38 GPa, grains show a pervasive fracturing, as seen

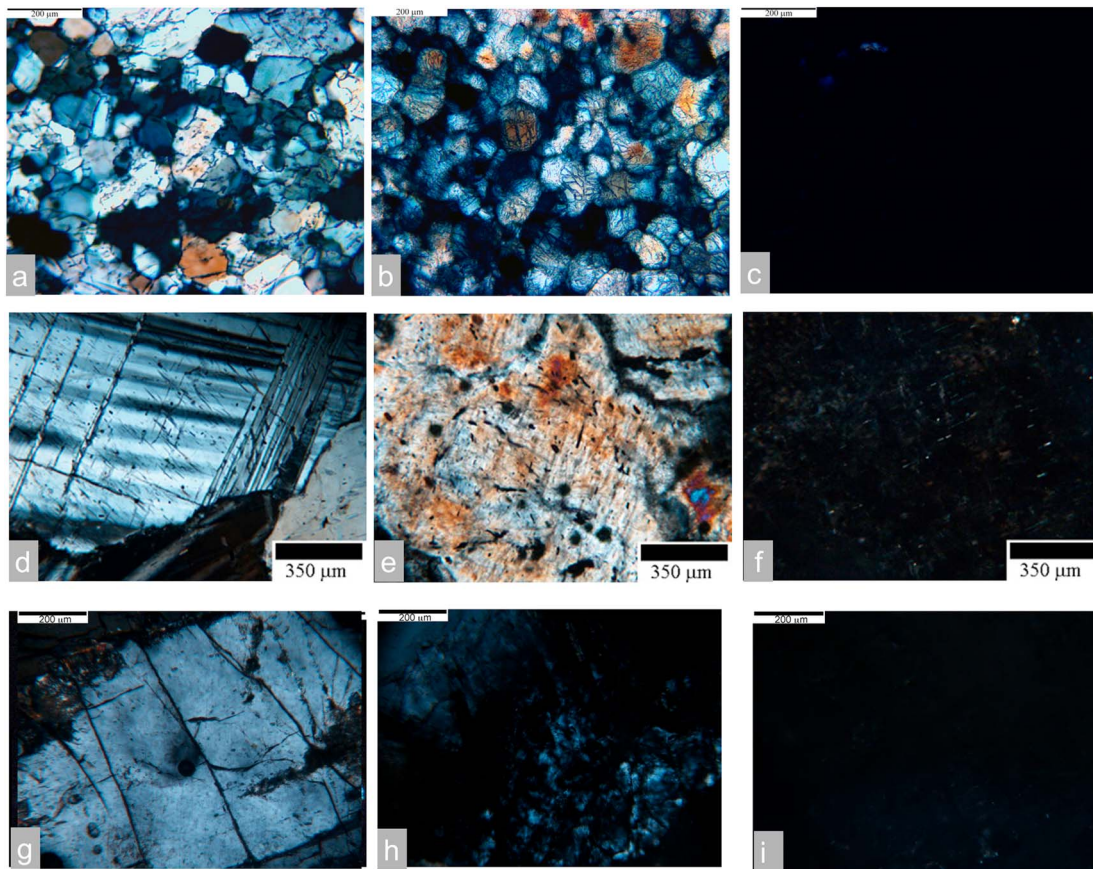


Figure 2. Cross-polarized photomicrographs of (top row) albite, (middle row) andesine, and (bottom row) bytownite at different shock pressures. (a) Unshocked, (b) 27.8 GPa, (c) 55.8 GPa, (d) unshocked, (e) 28.4 GPa, (f) 56.5 GPa, (g) unshocked, (h) 27.0 GPa, and (i) 56.3 GPa.

optically as nonplanar, open fractures crossing the majority of grains. 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 (Figures S37-A and S38-A). By 55.0 GPa, albite is fully optically amorphous (Figures 1c and 2c).

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 (i.e., “PDFs”). The fractures are irregular, nonplanar open fractures, which crosscut the majority of the grains. At 35.3 and 47.5 GPa, individual grains show patchy extinction and mosaicism (Figures S23-A to S25-A). Between 50.0 and 53.0 GPa, andesine grains are uniformly isotropic on an individual grain level (i.e., not patchy or partially isotropic grains) but not every grain appears isotropic. At 55.6 GPa, all grains are fully optically isotropic (Figure 2f).

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 38.2 GPa exhibit mosaicism and are heterogeneously shocked with multiple domains retaining their birefringence (Figures 1h and 2h). Above 38.2 GPa, bytownite is fully optically amorphous (Figures S10-A to S12-A).

5.2. Infrared Spectroscopy

5.2.1. Overview

Figure 3 shows photomicrographs of the three plagioclase samples at the three pressures (0, ~27, and ~56 GPa) annotated with the numbered locations from which single-point spectra were acquired with the MCT, DTGS, and Raman spectrometers. Plane-polarized thin section images were used to guide the selection of locations for which samples showed little obvious petrographic heterogeneity to the eye. Figure 4 shows

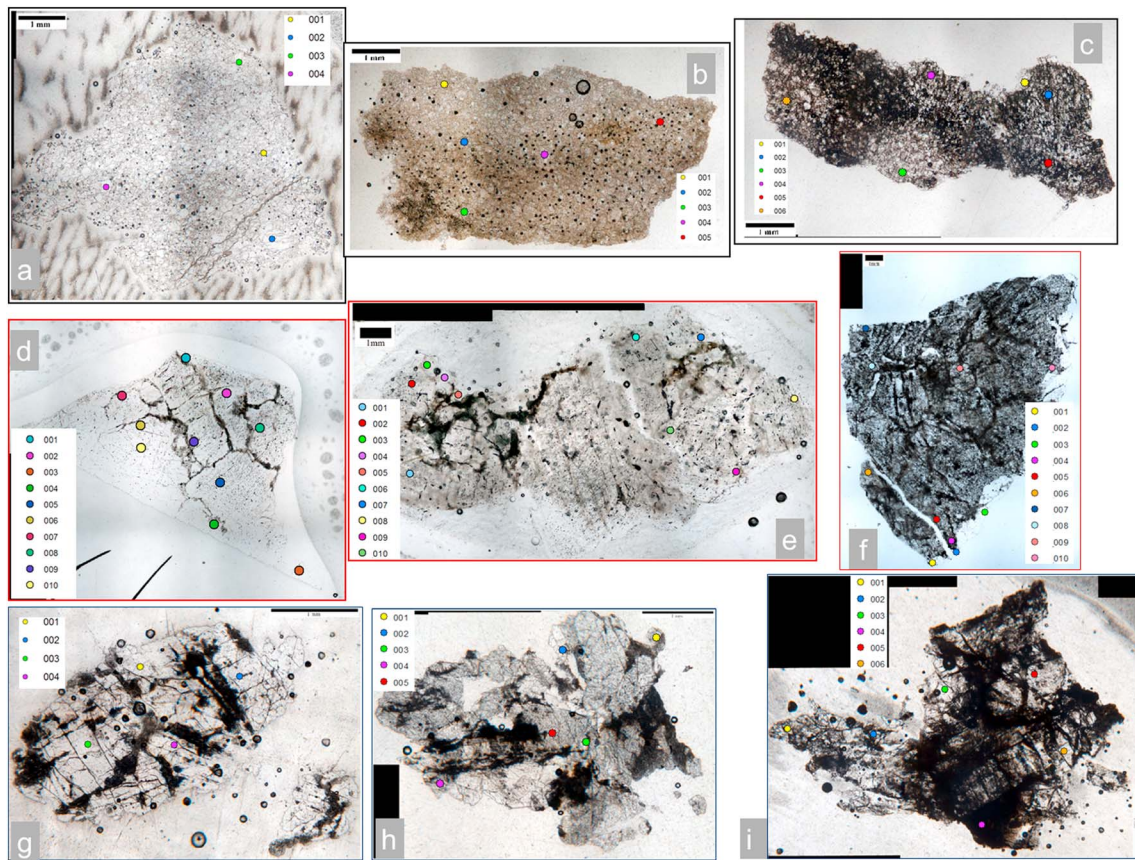


Figure 3. Photomicrographs showing numbered locations from which MCT, DTGS, and Raman point spectra were acquired (cf. Figures 8 and 13), shown as (top row) albite, (middle row) andesine, and (bottom row) bytownite at (a) unshocked, (b) 27.8 GPa, (c) 55.8 GPa, (d) unshocked, (e) 28.4 GPa, (f) 56.5 GPa, (g) unshocked, (h) 27.0 GPa, and (i) 56.3 GPa.

representative DTGS spectra from some of those locations, where the unshocked sample plots also include laboratory plagioclase spectra (Christensen et al., 2000) scaled for comparison.

Figures 5–7 show spectral parameter images generated from the 2-D hyperspectral images for albite (Figure 5), andesine (Figure 6), and bytownite (Figure 7). The three columns in each figure correspond to the three pressures (0, ~27, and ~56 GPa). The false-color images (top rows in each figure) were constructed using three spectral bands to emphasize spectral variability within the scene (band locations shown as vertical lines in Figure 4 unshocked sample plots). Numbered locations correspond to regions from which spectra were extracted (Figure 8, discussed below). The second row in each figure shows “band depth” maps (more accurately, reflectance peak maps) of one of the main reflectance peaks (1,149, 1,142, and 1,107 cm^{-1} , respectively, for Figures 4–6). The third row shows the ratio of the two main reflectance peaks.

Figure 8 shows spectra extracted from the 2-D hyperspectral images for the numbered locations identified in Figures 5–7. Unshocked sample plots also include laboratory plagioclase spectra collected at Arizona State University (Christensen et al., 2000) scaled for comparison. The reference unshocked spectra were converted from emissivity (using $1 - \text{emissivity}$). Selected locations sampled both the dominant regions in the sample (typically green to yellow portions of the false-color images), as well some minor phases that are most evident in the bytownite samples. Also shown (in white) is the average spectrum of the entire sample observed in the 2-D image.

Figure 9 shows the average spectra for all experimentally shocked samples obtained from the 2-D images, most of which are consistent with the macroscale observations acquired of these samples (Johnson, 2012; Johnson et al., 2002, 2003). The 2-D hyperspectral images allow more detailed investigation of the microscale variations. Figure 10 demonstrates how the average band depth parameters vary for each plagioclase, as well

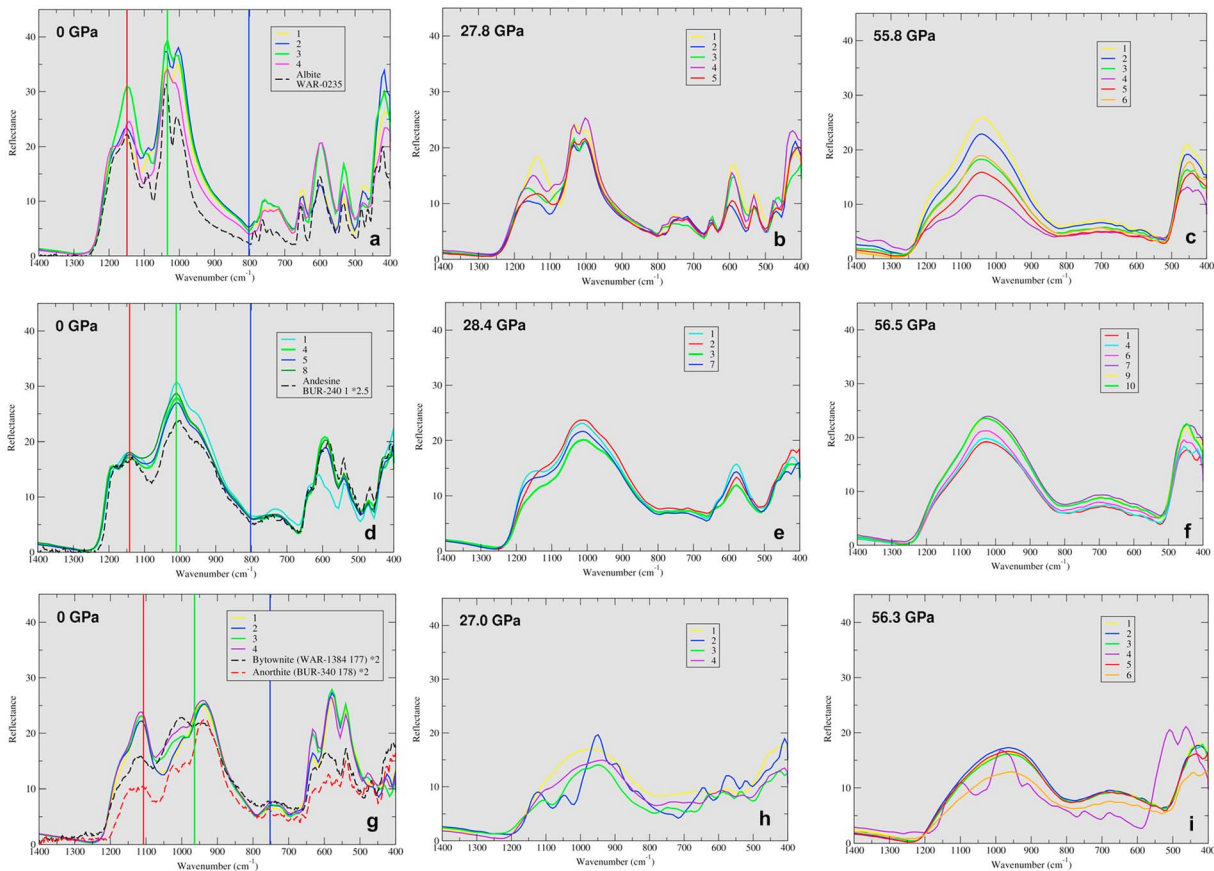


Figure 4. Point spectra acquired using DTGS detector for numbered locations shown on Figure 3 for (top row) albite, (middle row) andesine, and (bottom row) bytownite at pressures shown. Colors of spectra correspond to colors of points on Figure 3. For unshocked sample spectra plots, laboratory plagioclase spectra from Christensen et al. (2000) are included (dotted lines), converted to reflectance and multiplicatively scaled by the factor shown in the legend for each spectrum for ease of comparison. Grain sizes for each lab spectrum is 710–1,000 μm (Christensen et al., 2000). Colored vertical lines in the 0 GPa plots designate wavenumber positions used for spectral parameter products shown in Figures 5–7; the line colors denote wavenumbers in false-color images.

as their standard deviations, as a function of shock pressure. As discussed below, these variations provide insights regarding the homogeneity of the samples analyzed and the effectiveness of spectral parameters as measures of shock state.

5.2.2. Albite

DTGS spectra (400 to 1,400 cm^{-1}) of unshocked albite exhibit peaks near 1,149, 600, and 416 cm^{-1} , and a strong doublet near 1,034 and 1,002 cm^{-1} (Figure 4a). Multiple spots on the same sample show that the relative intensities and exact location of these peaks can vary from differences in crystal orientation (cf. Figure 11 and discussion in section 6.3), as emphasized by the mottled nature of the 2-D MCT (700–1,400 cm^{-1}) spectral parameter images (Figure 5) and discussed further below. However, as shown in the supporting information, none of the MCT or DTGS spectra vary appreciably from an albite-like mineralogy, consistent with the homogeneous starting nature of the albite-rich rock (Johnson et al., 2003). In Figures 9 and 10, albite spectra show minor changes up to about 31.4 GPa, beyond which the 1,034 and 1,149 cm^{-1} peaks diminished with increasing pressure. At pressures between 34.8 and 44.6 GPa, the doublet at 1,002–1,034 cm^{-1} began to merge, and the peak near 600 cm^{-1} began to broaden and decrease in intensity. At 50.0 GPa, the peak near 1,149 cm^{-1} disappeared, and the shorter wavenumber peaks merged to form one broad peak centered near 425 cm^{-1} . At 55.8 GPa, only broad peaks near 1,040 and 450 cm^{-1} remained, indicating a transition to an amorphous material (Figures 4c and 8c).

5.2.3. Andesine

DTGS spectra of unshocked andesine exhibited peaks at 1,142, 1,011, 650, and 595 cm^{-1} (Figure 4d). As shown in Figures 9 and 10, spectral variations were minor until about 26.4 GPa, at which point the

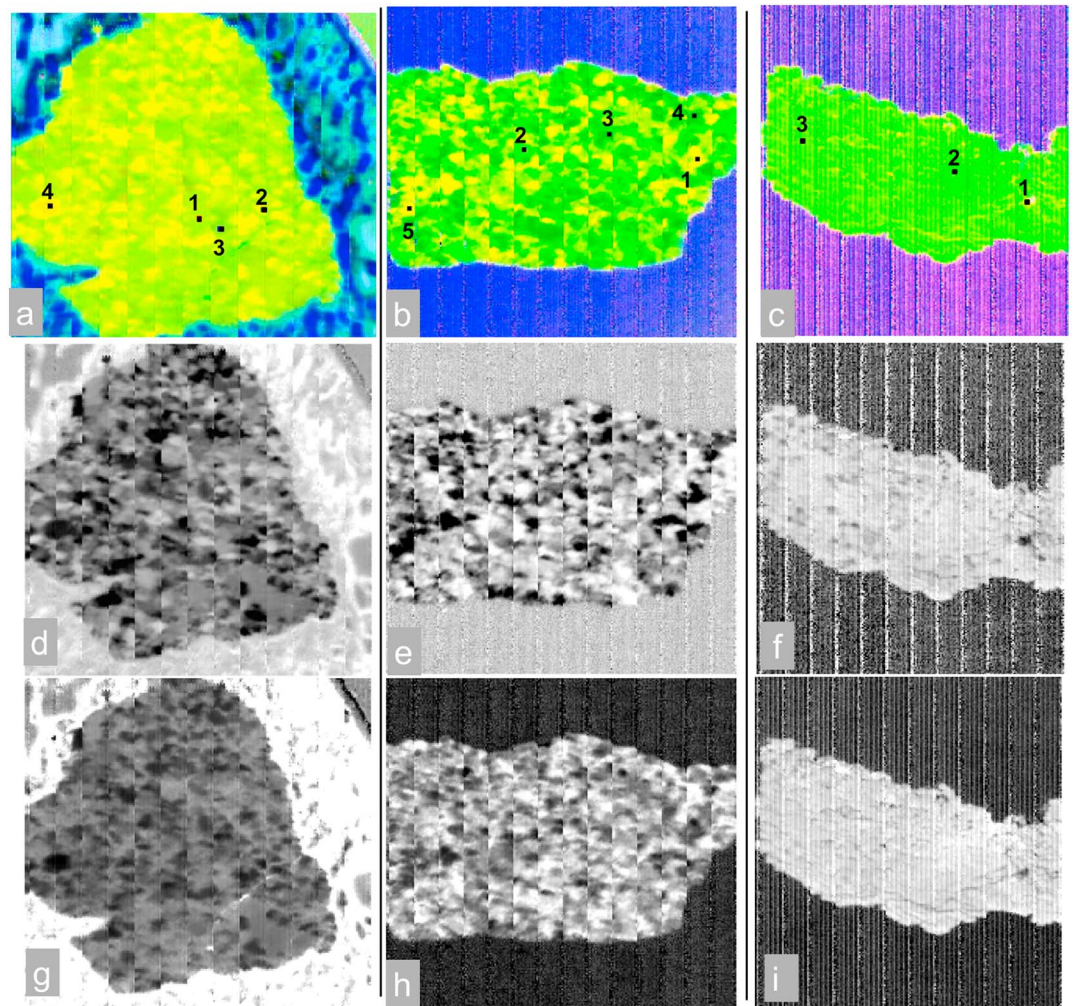


Figure 5. Albite spectral parameter images for (top row) false-color (using red = $1,149\text{ cm}^{-1}$, green = $1,034\text{ cm}^{-1}$, and blue = 802 cm^{-1}), (middle row) $1,149\text{ cm}^{-1}$ band depth, and (bottom row) $1,034/1,149\text{ cm}^{-1}$ ratio at (left column) 0 GPa, (middle column) 27–28 GPa, and (right column) ~56 GPa. Numbered points in false-color images designate approximate areas from which spectra were extracted (Figure 8).

$1,142\text{ cm}^{-1}$ peak progressively decreased in intensity. At 28.4 GPa and higher pressures, the peaks near $1,142$ and $1,011\text{ cm}^{-1}$ merged to form a broad peak near $1,012\text{ cm}^{-1}$ and a shoulder near $1,150\text{ cm}^{-1}$. The lower wavenumber peaks merged to a single peak near 586 cm^{-1} . After 33.8 GPa, the 586 cm^{-1} peak disappeared and gave way to a low, broad peak centered near 670 cm^{-1} and a prominent peak near 425 cm^{-1} . At the highest pressure (56.5 GPa), two prominent residual peaks occur near 1030 cm^{-1} and 445 cm^{-1} (Figures 4f and 8f). As with the albite data, samples may exhibit variable peak locations owing to crystal orientation effects, as discussed below (e.g., Figure 6a). A few of the MCT or DTGS spectra presented here (and in the supporting information) are more consistent with augite than andesine (e.g., spectra locations #4 in Figures 8e and 8f and the black spectra in Figures S25-E and S28-E), and this identification was confirmed with the optical microscope.

5.2.4. Bytownite

DTGS spectra of unshocked bytownite exhibited peaks near $1,103$, 964 , 630 , 580 , and 540 cm^{-1} (Figure 4g). Minor spectral variations occurred beginning near 21.0 GPa, at which point the 964 and $1,107\text{ cm}^{-1}$ peak began to decrease. By 29.3 GPa multiple shorter-wavenumber peaks merged to form a peak near 425 – 435 cm^{-1} , and the $1,107\text{ cm}^{-1}$ peak merged with 964 cm^{-1} peak to form a single peak near 952 cm^{-1} (Figures 4i and 8i), consistent with observations of the high-compression and shock-densified anorthite

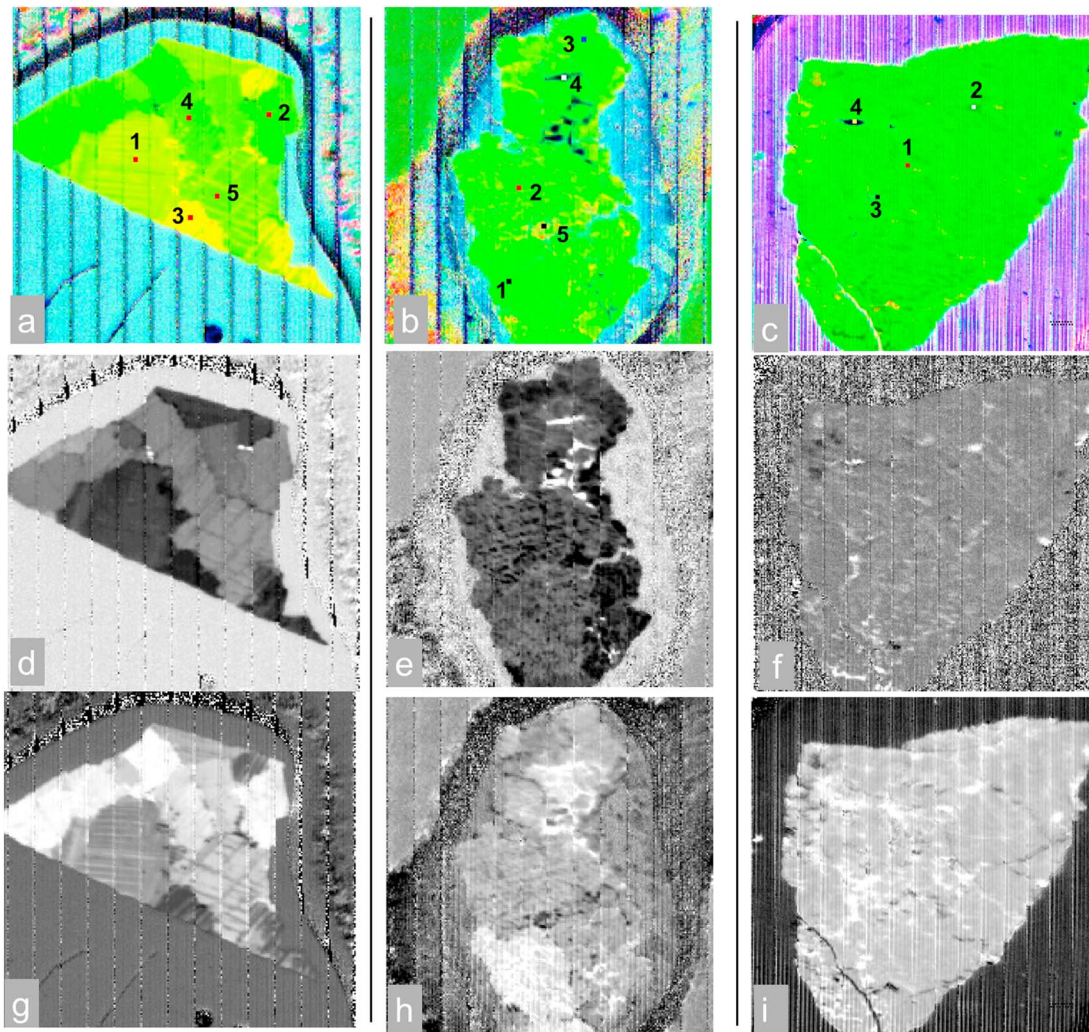


Figure 6. Andesine spectral parameter images for (top row) false-color (using red = $1,142\text{ cm}^{-1}$, green = $1,011\text{ cm}^{-1}$, and blue = 802 cm^{-1}), (middle row) $1,142\text{ cm}^{-1}$ band depth, and (bottom row) $1,011/1,142\text{ cm}^{-1}$ ratio at (left column) 0 GPa, (middle column) 27–28 GPa, and (right column) ~56 GPa. Numbered points in false-color images designate approximate areas from which spectra were extracted (Figure 8).

glasses studied by Reynard et al. (1999) and (Daniel et al., 1997). Beyond that pressure, few changes were observed in the peak positions or strengths (Figure 10), other than those associated with the type of crystal orientation effects observed for albite and andesine samples, or from minor alteration minerals. Examples of the latter can be seen for clinozoisite in Figure 8g (spectra location #1 (mixed with quartz) and #2) and Figure 8i (spectra #2, 6, and 7), and for quartz in Figure 8h (spectrum #1). The minor contribution of such alteration phases can be appreciated by comparing the average spectrum from each 2-D image in Figure 8 to the typical plagioclase spectra (e.g., locations #1 and #4 in Figure 8i).

5.3. Raman Spectroscopy

5.3.1. Overview

Figure 12 shows representative Raman spectra of the unshocked samples, with prominent Raman peak lines annotated. The most prominent peaks (~ 580 and 510 cm^{-1}) are associated with the Group I (SiO_4 tetrahedra) region (cf. Freeman et al., 2008). Additional peaks at ~ 290 , 410 , and 560 cm^{-1} occur in the groups II (lattice vibrations) and IV (deformation vibrations) regions for all samples, but only albite and bytownite include significant peaks in the group V (Si-O-Al stretching vibration) region (978 cm^{-1}).

Figure 13 shows Raman spectra for the three plagioclase samples at three pressures for the locations noted in Figure 3. Similar plots for all experimentally shocked samples are shown in the supporting information to this

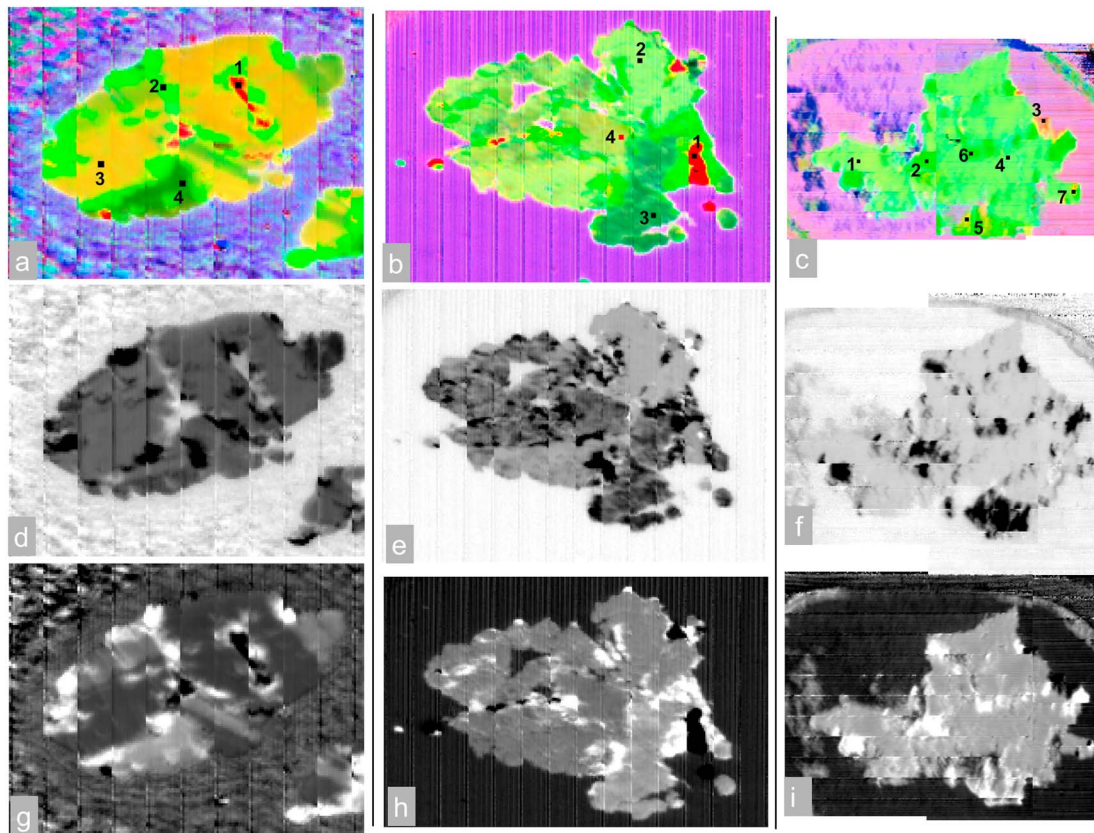


Figure 7. Bytownite spectral parameter images for (top row) false-color (using red = $1,107\text{ cm}^{-1}$, green = 964 cm^{-1} , and blue = 752 cm^{-1}), (middle row) $1,107\text{ cm}^{-1}$ band depth, and (bottom row) $964/1,107\text{ cm}^{-1}$ ratio at (left column) 0 GPa, (middle column) 27–28 GPa, and (right column) ~56 GPa. Numbered points in false-color images designate approximate areas from which spectra were extracted (Figure 8).

paper. Figure 14 shows for each plagioclase spectrum the intensity of three major Raman peaks at several locations on each sample as a function of shock pressure. Figure 15 plots the standard deviation of those values at each pressure to gauge the degree of homogeneity of the Raman spectra throughout a given sample with increasing shock state. Figure 16 plots the ratio of the two major Raman group I peaks at the same locations on each sample as a function of pressure.

5.3.2. Albite

Micro-Raman spectra of albite samples shocked up to 50.0 GPa show characteristic peaks at ~ 291 , ~ 479 , and 507 cm^{-1} (Figures 13a–13c). Additional peaks near 208, 251, 330, and 761 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 (Figure 14a), particularly the 507 cm^{-1} peak. The general decrease in standard deviations of the peak intensities demonstrates the increasing homogenization of the samples with increasing shock pressure (Figure 15). Similarly, up to 50 GPa, there is a general trend of the $479/507\text{ cm}^{-1}$ peak ratio approaching unity. Only the sample shocked to 55.8 GPa shows Raman spectra indicative of an amorphous material, specifically the broad peak near 485 cm^{-1} . As shown in the Supporting Information (Figures S29–D to S39–D), the albite Raman spectra do not vary greatly across the samples, consistent with the homogeneous nature of the starting material.

5.3.3. Andesine

Micro-Raman spectra of andesine samples show characteristic major peaks at ~ 287 , ~ 480 , and 510 cm^{-1} (Figures 13d–13f), with additional peaks near 410 and 571 cm^{-1} . In general, increasing shock level causes a decrease in peak intensity, starting with the low Raman shift peaks, leading toward a pattern showing just a broad peak near 487 cm^{-1} above 33.8 GPa. The major peaks persist to the 24.9 GPa sample, after which

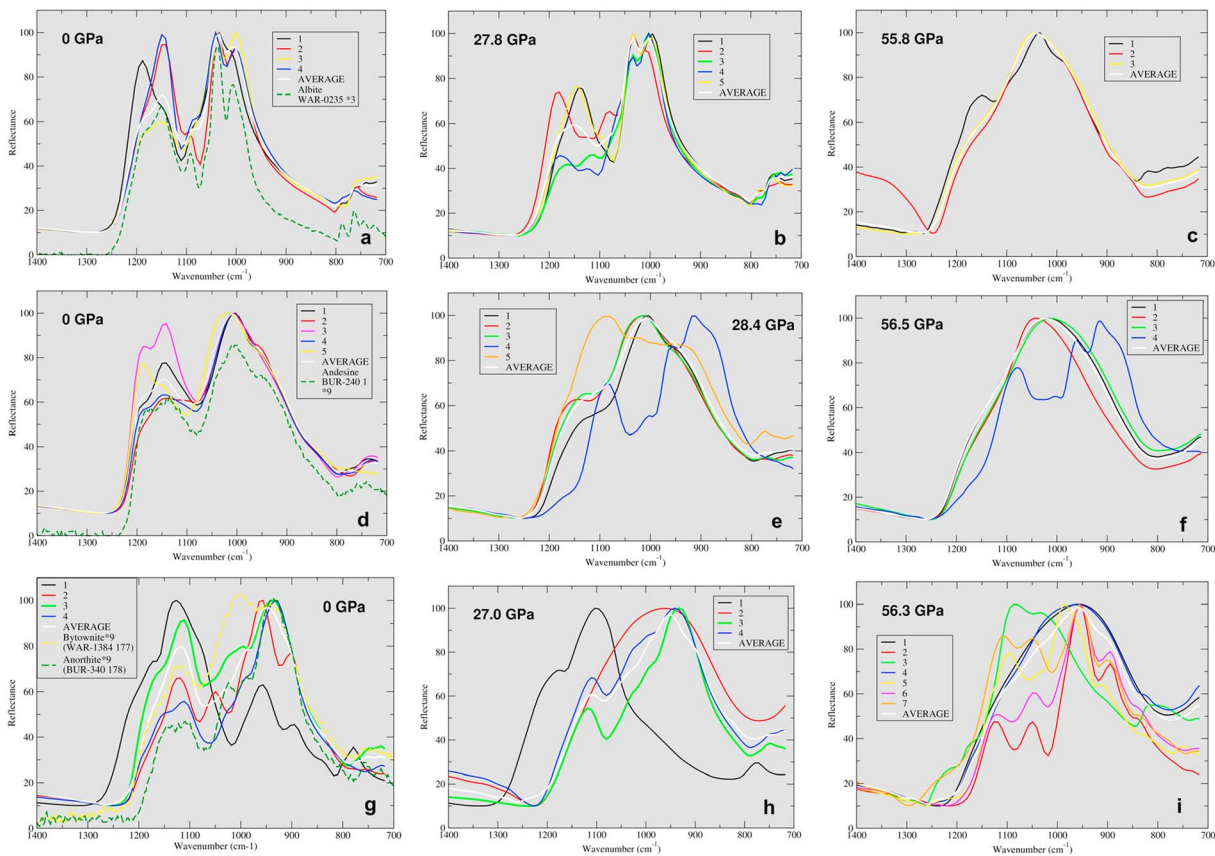


Figure 8. Spectra extracted from 2-D MCT hyperspectral images of (top row) albite, (middle row) andesine, and (bottom row) bytownite at pressures shown. Numbered locations correspond to those shown on Figures 5–7, corresponding both to plagioclase regions in the sample (typically green to yellow portions of the false-color images), as well as some minor phases. Each spectrum represents a 3×3 -pixel region. Average spectra for entire sample shown in white (cf. Figure 9). For unshocked sample spectra plots, laboratory plagioclase spectra from Christensen et al. (2000) are included (dotted lines), converted to reflectance and multiplicatively scaled by the factor shown in the legend for each spectrum for ease of comparison.

the $287 \Delta\text{cm}^{-1}$ peak disappears. Above 24.9 GPa, the samples show a decrease in overall intensity of peaks (Figure 14b) and their standard deviations progressively decrease (Figure 15b). The $480/510 \Delta\text{cm}^{-1}$ peak ratio increases overall with pressure (Figure 16). As shown in the Supporting Information, within each sample some of the individual spots retain some crystalline peaks at higher pressures. This leads to the scatter observed in Figures 14–16, which is a testament to the unequal but progressive amorphization of grains within the samples. We note that among all the andesine Raman spectra, only two were not representative of plagioclase (3508_001,003; Figure S16-D). Their Raman spectra were similar to alteration minerals such as hydrated iron sulfate.

5.3.4. Bytownite

Micro-Raman spectra of bytownite samples show characteristic major peaks at ~ 285 , ~ 484 , and $504 \Delta\text{cm}^{-1}$ (Figures 13g–13i), with additional peaks near 407 and $561 \Delta\text{cm}^{-1}$. Broader peaks in the group V (Si–O–Al stretching vibration) region occur near 683, 787, and $978 \Delta\text{cm}^{-1}$. Samples show a generally decreasing trend in peak intensities and their standard deviations (Figures 14c and 15c), and an increase in the $484/504 \Delta\text{cm}^{-1}$ peak ratio. Between 25.5 and 38.2 GPa, samples show a loss of peaks below $300 \Delta\text{cm}^{-1}$, and two broad peaks centered near 500 and $982 \Delta\text{cm}^{-1}$. These samples, however, are quite heterogeneous and exhibit regions that retained some crystallinity, as shown by the residual discernible peaks near 484 and $504 \Delta\text{cm}^{-1}$ in some locations and pressures. Above 38.2 GPa the samples exhibit only broad peaks near 500 and $996 \Delta\text{cm}^{-1}$ and are relatively homogenous, without regions that retained any crystallinity. The original bytownite-rich sample contained ~ 10 – 15% pyroxenes and alteration minerals such as clinozoisite (Johnson et al., 2002; Therkelsen, 2002; Therkelsen et al., 2002). Indeed, a small number of Raman spectra shown in the supporting information

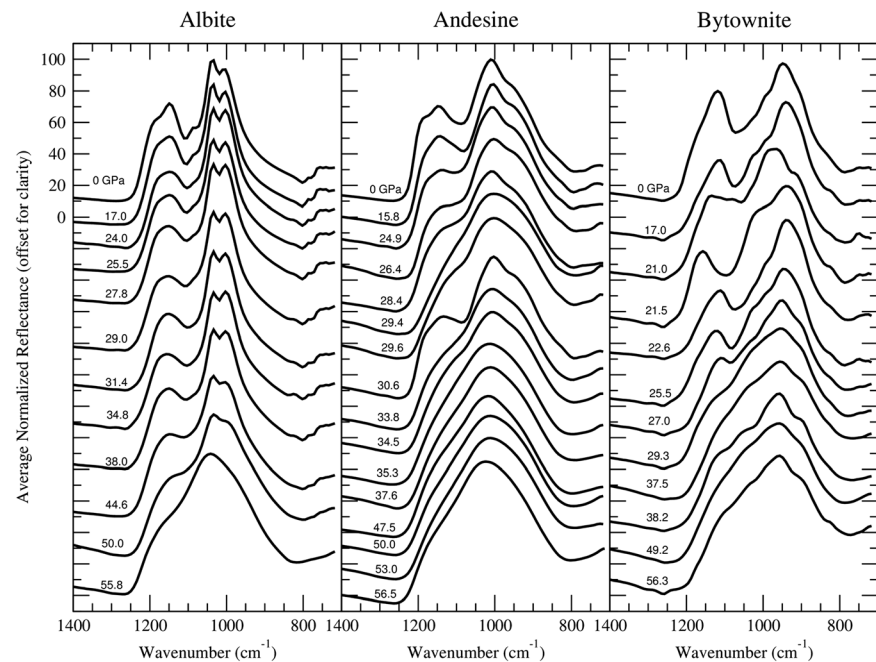


Figure 9. Average spectra extracted from 2-D MCT hyperspectral images for each plagioclase, offset and labeled with peak shock pressure.

are consistent with hydrated iron sulfate (3156_003,005; Figure S2-D), clinozoisite (3155_004; Figure S5-D; 3149_004; Figure S11-D), or quartz (3148_005; Figure S9-D).

6. Discussion

6.1. Petrography

Thin sections of all three plagioclase compositions exhibit a decrease in birefringence with increasing pressure, consistent with a general trend of disordering. Interestingly, however, no typical shock metamorphic microstructures (e.g., PDFs or feather features) are observed in any samples. For example, 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 & Koeberl, 2010). The 22.6 GPa bytownite sample shows microfaulted, offset and slightly rotated twins (Figure S5b-A). This texture is not considered diagnostic of shock metamorphism (French & Koeberl, 2010) but does occur readily in natural impactites, such as reported at Lapparjarvi (Reimold, 1982) or at the Gardnos impact structure (French et al., 1997). In the experimentally shocked bytownite, the offset twins are clearly shock induced. 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 & 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 & Reimold, 1996), are not seen in any of the investigated samples. IR and Raman analyses of these samples do show they have been disordered structurally, yet PDFs are not visible under the optical microscope. PDFs were expected to occur in these samples because PDFs in quartz have been produced experimentally at these pressure ranges in Huffman & Reimold (1996) and Langenhorst (1994b). Quartz is very rare in our samples, occurring only in the bytownite samples (shown as red in false color maps in the supporting information) and only occurs in two of the thin sections. Neither of these show PDFs, but in both cases, the quartz grains are on the edge of the sample, and likely are not representative of shock conditions in the broader sample. Despite significant study of experimentally produced PDFs in quartz, PDFs in experimentally shocked feldspars have not been studied in detail. Huffman and Reimold (1996) report PDFs in quartz and feldspar in experimentally shocked granitic and quartzitic samples, but only show photomicrographs

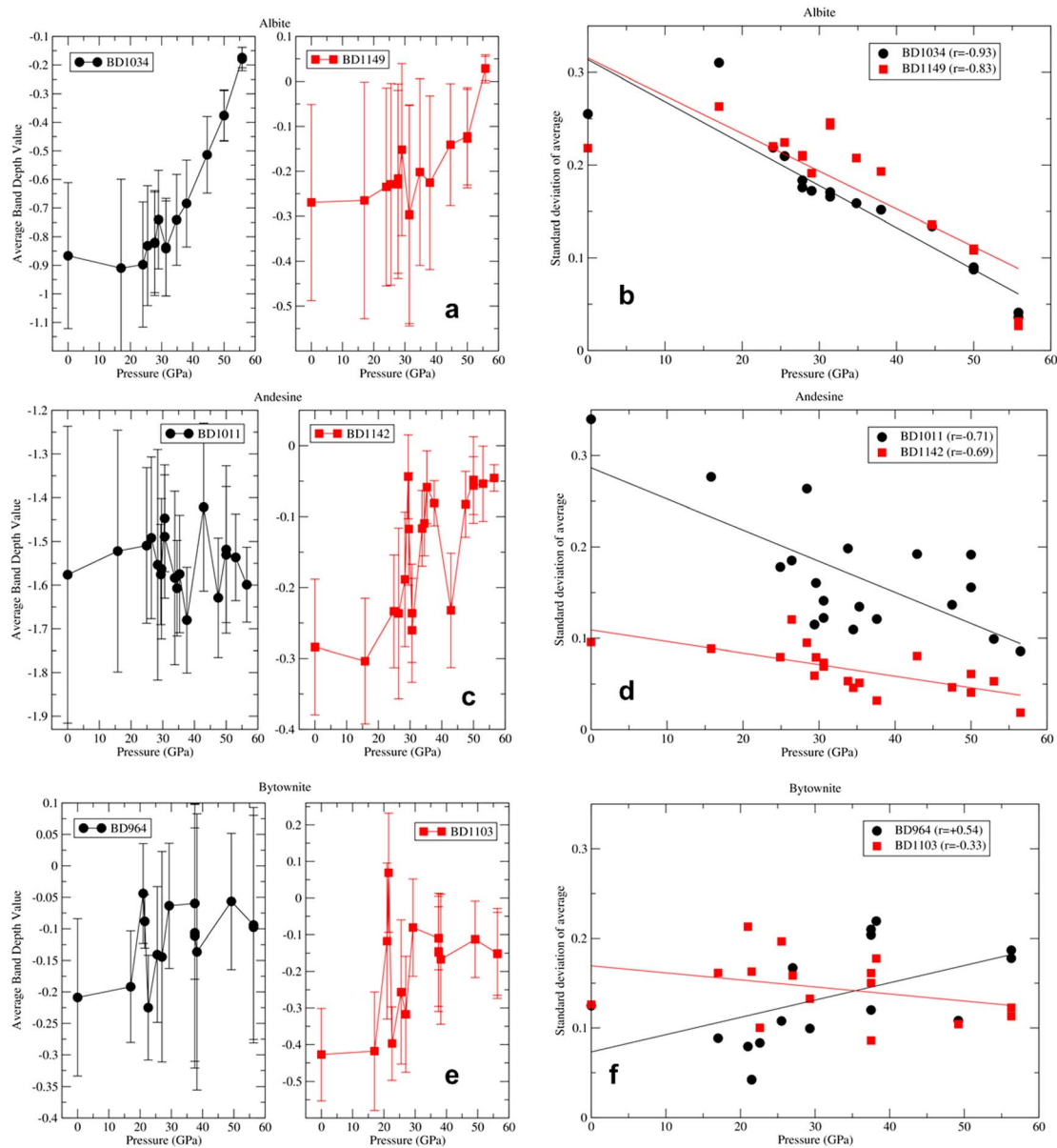


Figure 10. Average band depth parameters and their associated standard deviations plotted for (a and b) albite, (c and d) andesine, and (e and f) bytownite. Albite is the most homogeneous sample, as evidenced by the clear decrease in $1,034\text{ cm}^{-1}$ band depth standard deviation with increasing pressure (linear correlation coefficients shown in legends). For comparison, the more heterogeneous bytownite samples show weaker correlations.

of PDFs in quartz. Ostertag (1983) also reports PDFs in experimentally shocked single crystals of plagioclase, but again does not show photomicrographs. Feldspars are more optically (and chemically) complex than quartz, and so it is possible that development of PDFs in feldspar is more complicated than in quartz or requires a much more unique set of conditions. Likely, these defects are present (as suggested by the IR and Raman data present here) but not visible optically. Additional characterization work at microscale and nanoscale is necessary to fully understand how the disordering is manifested at these scales, and under these experimental conditions.

The most prominent petrographic texture seen in thin section from all samples here is an apparent darkening of individual minerals 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

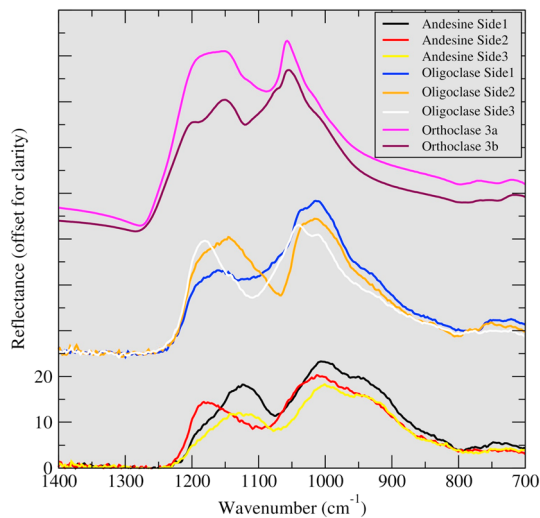


Figure 11. Comparison of laboratory spectra of plagioclase crystals acquired at different crystallographic orientations. Andesine and oligoclase data acquired by Ruff (1998); orthoclase spectra from Salisbury et al. (1991).

controversial, and often suggested to have to do with finely disseminated sulfides within grains and concentration of Fe-metals or due to frictional melting (Bischoff et al., 2006; Britt & Pieters, 1994). Shock darkening in tectosilicates has been reported in natural terrestrial impactites, such as the “black quartzite” at the Gardnos, Manson, and Roter Kamm impact structures (French et al., 1997; Koeberl et al., 1996; Reimold & Miller, 1989). Specifically at Gardnos, the darkening is visible at both hand sample and individual mineral scale, particularly apparent as subgrain darkening of feldspars, despite undarkened quartz. The specific crystallographic structure and mechanism of the darkening seen here are still largely unknown, but it has been suggested to be an optical effect due to a dramatic increase of dislocations at the atomic level.

6.2. Amorphization Pressures

Based on our spectroscopic analyses, we place an amorphization onset 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. We note that this applies only to well-crystalline anorthositic rocks at room temperature, with near-zero porosity. Single crystals or highly porous rocks will have significantly different amorphization points. This is 5–10 GPa

lower than where the thin sections suggest that the samples are fully optically isotropic (Figure 2). 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 microspectroscopy.

One complication in assigning an amorphization pressure is that the amorphization occurs over a range of pressures. There are separate points for amorphization onset and amorphization completion, and these points can be substantially different. However, frequently previous studies have only indicated one amorphization point, which may contribute to the confusion and disagreement in the literature. Here we see this distinction both petrographically and in the infrared data. Petrographically, amorphization onset is noted as where individual grains become isotropic whereas the sample is not considered fully amorphous until all parts of all grains are isotropic. In infrared spectra, we can identify both the amorphization onset and

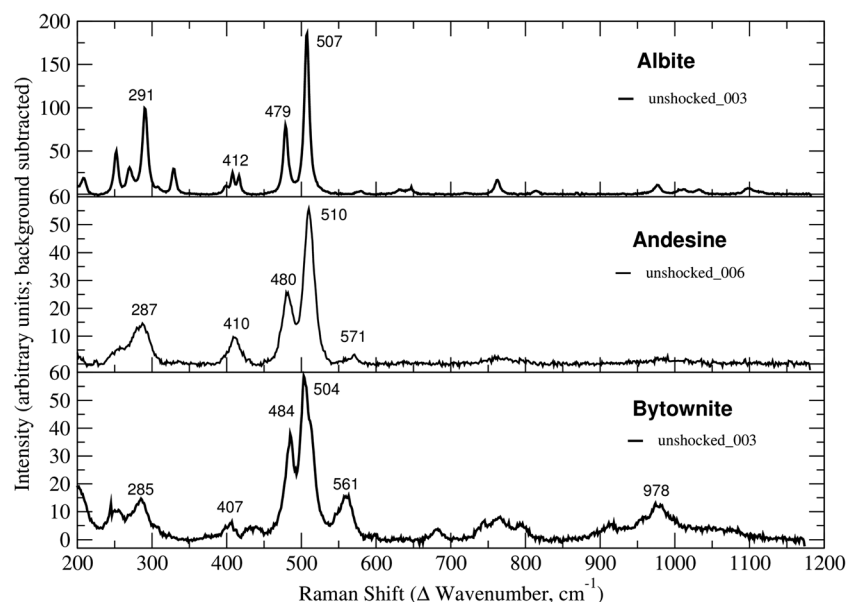


Figure 12. Raman spectra for unshocked plagioclase (specific sample located in Figure 3 shown in legend), with dominant spectral peak positions labeled.

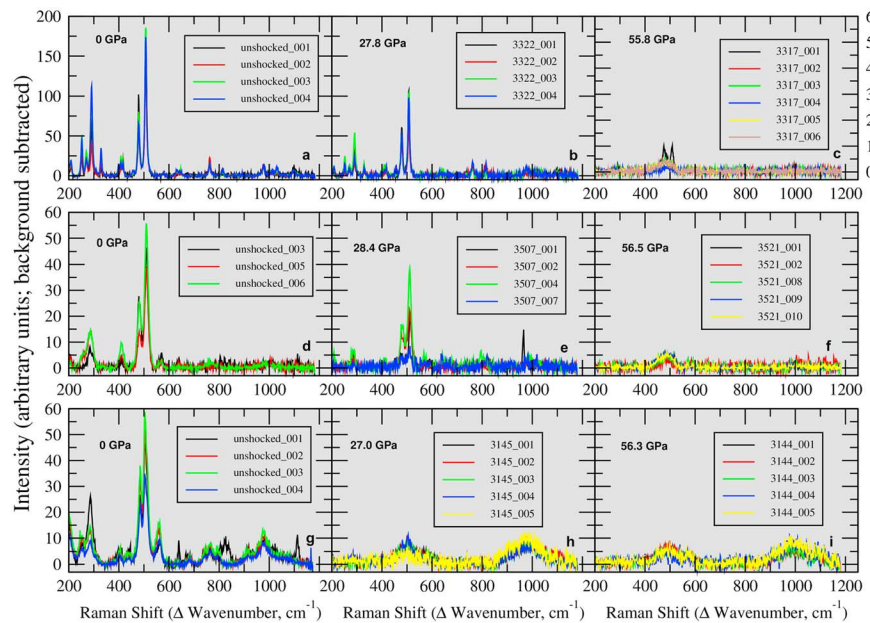


Figure 13. Raman spectra extracted from locations shown in Figure 3 for (a–c) albite, (d–f) andesine, and (g–i) bytownite at pressures shown.

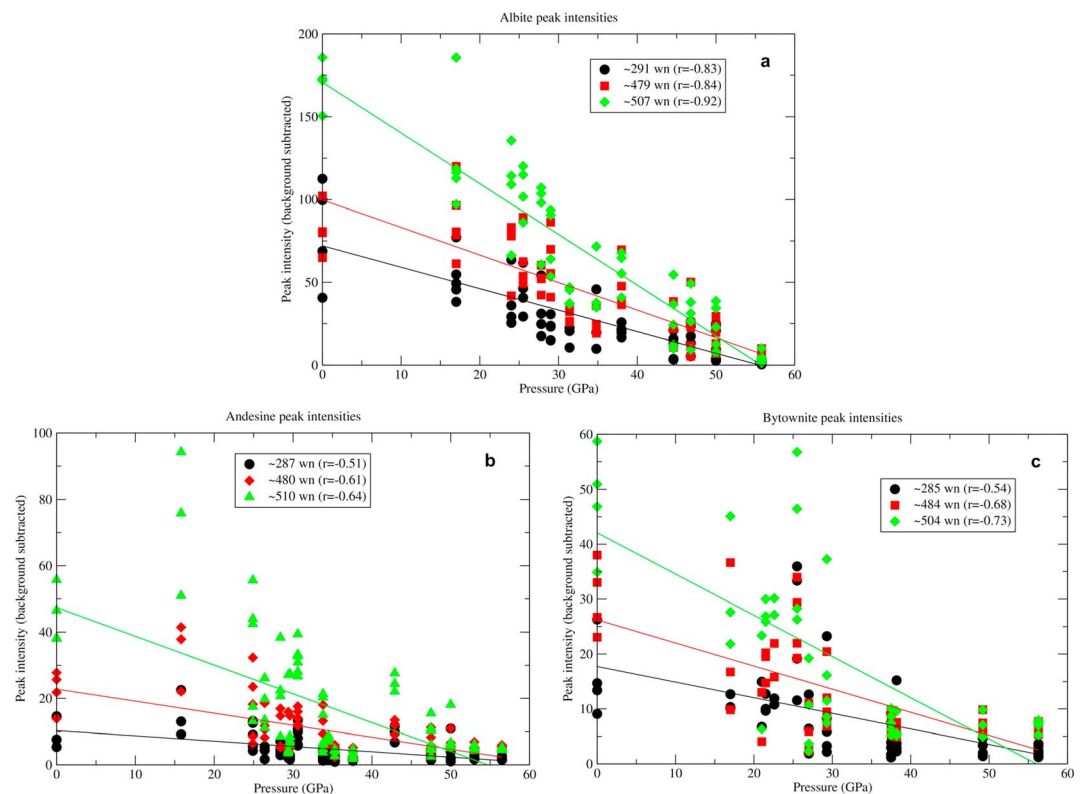


Figure 14. Raman peak intensities for specific wavenumbers for each plagioclase sample as a function of shock pressure, with linear correlations shown, for (a) albite, (b) andesine, and (c) bytownite.

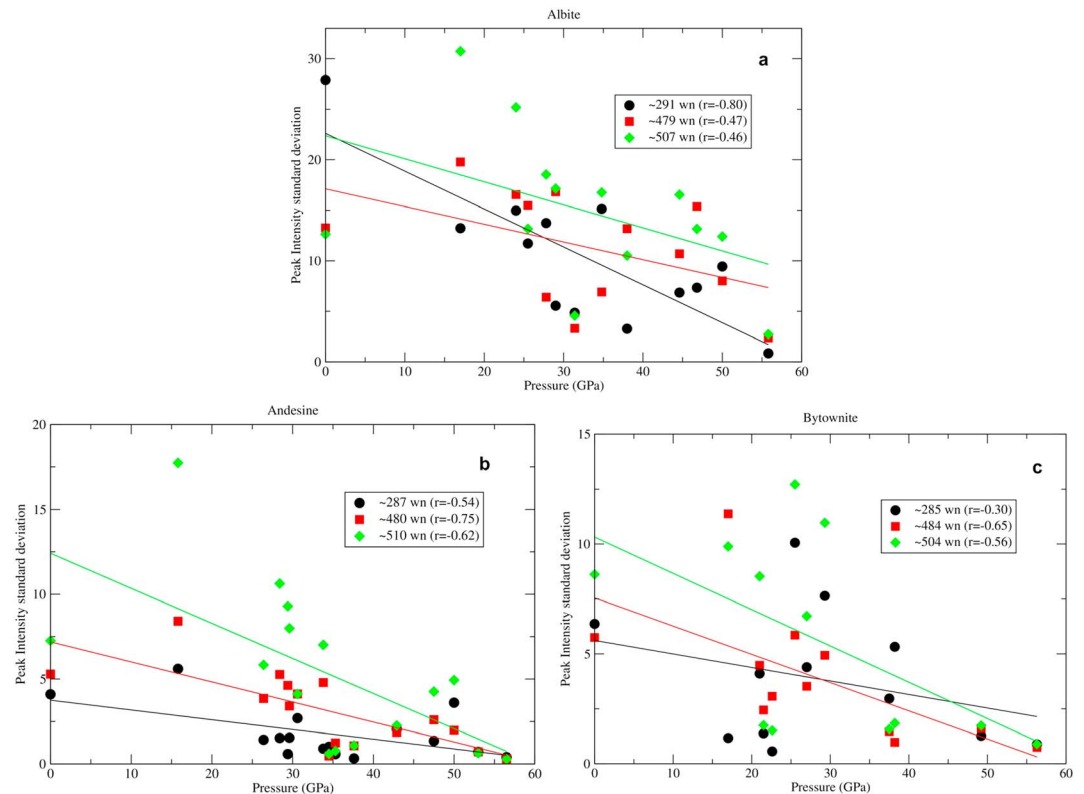


Figure 15. Standard deviations of Raman peak intensities (shown in Figure 14) as a function of pressure for (a) albite, (b) andesine, and (c) bytownite.

completion; however, this manifests itself slightly differently for albite than for andesine and bytownite. In andesine and bytownite, amorphization onset is identified by the loss of the high wavenumber peaks ($\sim 1,180 \text{ cm}^{-1}$), and amorphization completion is identified as having only one peak, without shoulders. In albite, amorphization onset is identified as the loss of the doublet near $1,000 \text{ cm}^{-1}$ and amorphization completion is identified as only one broad peak remaining. It is worth noting, however, that because albite remains crystalline to high pressure, only one sample was fully amorphous and therefore defining this is difficult.

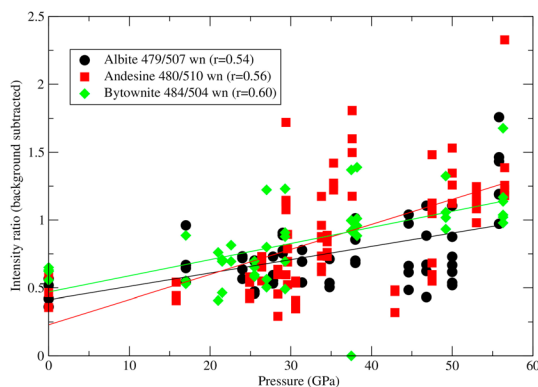


Figure 16. Peak ratios of dominant peaks of plagioclase samples for all Raman spectra as a function of shock pressure, with linear correlations shown.

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 was interpreted by Jaret et al. (2015) as indicative of remnant crystal orientation differences. For example, the bytownite samples shocked to 29.3 and 37.5–38.2 GPa show peak positions that vary across the samples by up to 40 cm^{-1} (Figures S8-C and S9-C). At 38.2, 49.2, and 56.3 GPa, however, that variation in peak position is not seen (Figures S10-C, S11-C, S12-C, 4i, and 8i), suggesting that the transition to complete amorphization of all plagioclase has not yet been reached.

Indeed, across all techniques, shocked sample spectra display significant variability (beyond that resulting from minor nonplagioclase components). Some areas remain crystalline while adjacent grains or subgrain domains become amorphous. The microscale heterogeneity seen here is similar to what is observed in naturally shocked impactites. There are several possible explanations for the observed microscale

heterogeneity. First, it could be due to heterogeneity within the shock wave itself (Fritz et al., 2017, and references therein). Second, it could be due to refractions and impedances as the shockwave crosses between grains, especially for adjacent grains of different composition such as observed particularly in the bytownite sample. Lastly, the heterogeneity in shock response could be due to orientation effects of the individual grains, given that 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.

Previous IR studies of shocked samples have required the use of large spot sizes on sample powders or averaged over large areas of the sample that would suppress any orientation effects. Indeed, the spectra average from each 2-D image (Figures 8 and 9) are very similar to the macroscale emissivity and reflectance spectra acquired of these samples (Johnson, 2012; Johnson et al., 2002, 2003). 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 impedances due to crystal orientation. Similarly in this study, total energy imparted could explain our observation that the highest shocked samples are relatively homogeneous compared to the other samples.

6.3. Effects of Crystal Orientation

The effects of crystal orientation on infrared spectra have been described briefly by previous workers (e.g., Christensen et al., 2000; Hecker et al., 2010; Klima & Pieters, 2006; Lane et al., 2002; Lyon, 1963; Martin et al., 2018). In Figure 11, we provide examples of infrared spectra of feldspar minerals acquired under different crystallographic orientations to illustrate the magnitude of the reflectance peak shifts. The andesine and oligoclase spectra were converted to reflectance from the emissivity spectra acquired by Ruff (1998), whereas the orthoclase spectra were hemispherical reflectance spectra from Salisbury et al. (1991). For andesine, the two main peak reflectances shift from 1,001 to 1,012 cm^{-1} and from 1,123 to 1,180 cm^{-1} . For oligoclase, the shifts are from 1,012 to 1,041 cm^{-1} and from 1,145 to 1,180 cm^{-1} . These shifts are similar to those observed in spectra extracted from plagioclase in the 2-D hyperspectral images above. This explains much of the variations observed in the 2-D spectral parameter images (Figures 5–7), with the exception of minor alteration phases or pyroxenes in the samples.

The heterogeneity at the small spatial scale observed here complicates efforts to use spectroscopy as a quantitative measure to determine shock level within samples. For example, although the main reflectance peaks in albite infrared spectra exhibit on average the clearest decrease with increasing shock pressure (Figures 10a and 10b), the standard deviations of each sample overlap substantially. Less clear trends in the andesine and bytownite samples (Figures 10d–10f) are affected to even greater degrees by these overlaps. Similarly, the plots of Raman plagioclase peak intensities and ratios (Figures 14–16) show a general decrease with pressure, but there is enough scatter within each sample that the ratio is not a unique indicator of shock level. It is possible to distinguish the highest shocked samples (e.g., >50 GPa) from unshocked or lower shock level samples. But at intermediate pressures, the ranges of peak intensities overlap with the adjacent pressures, suggesting that attempts to assign Raman intensity ratio values to specific shock pressures should be treated with caution (cf. Baziotis et al., 2013; Fritz et al., 2005).

Specific infrared and Raman spectral parameters are not unique to shock level as shown in Figures 10, 14, and 15. This heterogeneity within each sample likely results from a combination of one or more of the following: (i) the compositionally heterogeneous nature of the starting materials (e.g., interactions between the shock wave and materials of different densities within the sample), (ii) heterogeneity of crystal orientation within the sample, or (iii) the heterogeneous nature of the shock wave itself prior to interacting with the sample. For example, recent microscopic observations of the NWA 8159 shergottite by Herd et al. (2017) demonstrated that the partial amorphization of larger plagioclase crystals coincided with their proximity to shock veins. They noted that the deviatoric stresses and temperature gradients associated with shock vein margins likely resulted in a distribution of shock states in nearby plagioclase grains, consistent with the results of Daniel et al. (1997) and Kubo et al. (2010).

7. Conclusions and Future Work

Petrographically, the experimentally shocked plagioclases studied here appear to show slightly different characteristics than naturally shocked samples. Up to ~50 GPa, none of the bytownite, andesine, or albite

samples display typical shock induced microstructures (i.e., PDFs). 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.

Micro-Raman and micro-FTIR infrared spectra indicate that these samples undergo the expected trends in internal disordering. We interpret the amorphization onset pressure in these experimentally shocked anorthositic rocks with zero porosity to be 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. Amorphization completion occurs at >55 GPa for albite, ~47 GPa for andesine, and ~38 GPa for bytownite. These values are consistent with previous experiments, albeit under different experimental setups and spatial scales. For example, the progression of higher amorphization pressures for more sodic plagioclase is consistent with previous work (e.g., Huffman & Reimold, 1996; Johnson, 2012; Okuno, 2003; Ostertag, 1983). Although all techniques used here (IR, Raman, and optical petrography) place the amorphization region at the same shock level for a given plagioclase, heterogeneities in starting composition and/or shock propagation result in variable distribution of shock effects within the sample. General trends in degradation of both the IR and Raman spectra are readily observed. However, micro-spectroscopy does not provide unique indicators of shock state, and assigning spectral characteristics to a specific shock level should include substantial uncertainties, especially at intermediate pressures. Furthermore, these experimental amorphization values represent distinctly different strain rates and/or temperatures than those associated with natural impacts. Therefore, it may not be straightforward to assume that natural samples will become amorphous at this same pressure regime. Similarly, porosity, grain size, and water content can also influence the exact transformation conditions.

We will use the results from these microscale analyses of plagioclase in the next stage of our work, which will use the same techniques to study the experimentally shocked basaltic rocks from Johnson et al. (2007) and Jaret et al. (2018). This will enable better understanding of the microscopic effects of shock propagation through rocks with variable mineral types and grain sizes. Additionally, ongoing Raman observations are underway of the unshocked plagioclase samples subjected to static pressures using a diamond anvil cell apparatus (Jaret et al., 2015). These are providing useful insight regarding the relative magnitudes of pressures required for amorphization under static compression (diamond anvil cell) versus dynamic (shock) conditions. The combination of these studies will continue refining our understanding of the effects of high shock pressures associated with impact events on rocky bodies in the Solar System.

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