Unconventional high-pressure Raman spectroscopy study of kinetic and peak pressure effects in plagioclase feldspars

Melissa Sims^{1,2} · Steven J. Jaret^{1,5} · Jeffrey R. Johnson³ · Matthew L. Whitaker^{1,4} · Timothy D. Glotch¹

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Abstract

We present the results of a high-pressure semi-hydrostatic study of two plagioclase minerals, andesine and albite, using diamond anvil cells (DACs) to characterize in situ variations in Raman spectra under different static pressures. In this work, we also examined the kinetic effects on deformation at both long and short timescales through non-traditional experiments in which the DAC was either dropped or struck with a mallet. We examined the effects of strain rate, quench rate, and pressure duration on the Raman spectra of plagioclase. We observed that amorphization occurred in all the plagioclase samples we analyzed, and that amorphization onset and permanence differ depending on the composition, kinetics, energy input, and peak pressure. In andesine, samples pressurized above a peak pressure of 18 GPa, amorphization is permanent. Below this critical pressure, the phase has ‘memory’, and crystalline andesine reforms on decompression. Our findings suggest the presence of a thermodynamic energy well in andesine around 18 GPa, and we show that any additional energy input while close to 18 GPa results in amorphization becoming permanent. The effect of the energy well may be relevant for longer duration impacts. For such impacts, equilibrium state studies of deformation and phase formation were previously considered to be applicable. These experiments illuminating the presence of memory effects in plagioclase have implications for comparing static compression, in which samples are measured while under compression, with shock compression, for which samples are measured after decompression.

Keywords Kinetic study · Plagioclase · High-pressure Raman spectroscopy · Albite · Andesine

Introduction

The structure and transformation of plagioclase at extreme conditions (high-pressure, high-temperature) have been of interest in meteoritics since the discovery of “maskelynite” in the shocked meteorite Shergotty (Tschermak 1872). While the origin of maskelynite has been the subject of debate

(Gillet and El Goresy 2013), it is generally considered to be a diaplectic plagioclase glass transformed by solid-state processes during shock events (Arndt et al. 1982; Bunch et al. 1967; Diemann and Arndt 1984; Gillet and El Goresy 2013; Hörz and Quaide 1973; Jaret et al. 2015; Milton and de Carli 1963). These glasses are commonly observed in association with impact events (DeCarli and Jamieson 1961; Milton and de Carli 1963; Williams and Jeanloz 1989). Shock pressures experienced during impact cratering events can significantly alter the crystal structure of many minerals (Chao 1968; French and Short 1968). Amorphous plagioclase is used as the indicator for the petrographic type or shock stage S5, indicating pressures between 35 and 45 GPa (Stöffler 1971, 1972, 1974; Stöffler et al. 1991; Engelhardt et al. 1967). With increasing peak pressure in plagioclase, there is a progression of deformation from optical extinction to undulatory extinction and partial isotropization, to planar deformation fractures, and finally to planar deformation features (Stöffler 1971, 1972; Stöffler et al. 1991). At higher peak pressures, melting and/or high-pressure phase

✉ Melissa Sims
msims9@jhu.edu

¹ Department of Geosciences, Stony Brook University,
Stony Brook, NY 11794-2100, USA

² Department of Earth and Planetary Sciences, Johns Hopkins
University, Baltimore, MD 21218-2687, USA

³ Johns Hopkins University Applied Physics Laboratory,
Laurel, MD 20723-6005, USA

⁴ National Synchrotron Light Source II, Brookhaven National
Laboratory, Upton, NY 11973, USA

⁵ Department of Earth and Planetary Sciences, American
Museum of Natural History, New York, NY 10024, USA

transformations can occur (Stöffler 1971, 1972; Stöffler et al. 1991).

Traditionally, studies of structure and deformation in naturally shocked plagioclase (both terrestrial and extraterrestrial) have consisted of optical microscopy supplemented with X-ray, infrared, and/or Raman spectroscopy (Diemann and Arndt 1984; Fritz et al. 2005; Hörz and Quaide 1973; Jaret et al. 2014, 2015; Pickersgill et al. 2013; Velde et al. 1989; Sims et al. 2019) to better understand the shock and thermal history of meteorites and impactites (Bischoff and Stöffler 1992; Dence et al. 1977; Sharp and DeCarli 2006; Short 1970; and Stöffler et al. 1991). A number of researchers have conducted experimental studies intended to evaluate and understand deformation in plagioclase under known or calibrated conditions using either dynamic shock experiments, or static diamond anvil cell (DAC) as discussed in detail in Sims et al. (2019).

A critical note about experiments performed in the laboratory should be highlighted here: experimental shock pressures are of much shorter duration compared to those that occur in nature, whereas those from static compression are much longer (Langenhorst and Hornemann 2005). This is because the pressure at which plagioclase amorphizes is dependent on strain rate (Sims et al. 2019) and potentially on P–T path. The duration of peak pressure is not typically standardized and remains largely unstudied (Carl et al. 2017), as is quench rate, which can differ from compression rate (Langenhorst and Hornemann 2005; Sharp and DeCarli 2006). To investigate the dissimilarities between impact metamorphism and experimental conditions, we examine processes during both compression and decompression in this study, which have not previously been addressed. We study the effect of strain rate, quench rate, and pressure duration on potential phase memory effects, as discussed in previous studies (Daniel et al. 1997; Farber and Williams 1996; Jamet 1988; Sims et al. 2019; Strukov 1989).

Raman spectroscopy of plagioclase under pressure

This study focuses on using Raman spectroscopy at high pressure to study systematic changes in peak intensity to reveal the response of plagioclase to increasing pressures. Plagioclase has Raman-active vibrational modes belonging to the tetrahedra, tetrahedral framework, and lattice (Sharma et al. 1983). The Raman peaks of plagioclase were classified by Freeman et al. (2008) based on calculations from McKeown (2005) into five groups. The classifications are based on vibrational modes of the TO_4 tetrahedra (T is Al or Si). Group I features are due to stretching modes ($450\text{--}520\text{ cm}^{-1}$). Group II/III features are due to rotation/translational modes and include peaks from 240 to 300 cm^{-1} and from 150 to 210 cm^{-1} , respectively. Group IV features are due to deformation modes and are found from 550 to 830 cm^{-1} .

Group V includes anti-symmetric vibrational stretching modes that occur from ~ 875 to 1200 cm^{-1} . More detailed modeling of albite by Aliatis et al. (2017) recognized and assigned 39 modes and provided more specific information about the atomic vibrations and motions, with particular focus on the Na^+ configuration.

Multiple studies have used Raman spectroscopy as a measure of crystallographic deformation associated with progressive amorphization in response to compression (Fritz et al. 2005; Heymann and Hörz 1990). Velde et al. (1989) analyzed Raman spectra of three different feldspar compositions experimentally shocked from 21 to 54 GPa using both 488 nm and 514.5 nm lasers. They found that albite exhibited the greatest resiliency to shock pressure and suggested that the lattice of shocked albite responds differently between shock and static compression. Because memory effects do not occur in albite (Tomioka et al. 2010), the Na endmember of plagioclase, observation of amorphization on multiple members of the plagioclase system is necessary. Memory effects may not occur in albite possibly due to the differences in the degree of structural reorientation and amount of broken bonds (Mookherjee et al. 2016) between the plagioclase endmembers' proposed amorphous structures. Raman spectra of minerals subjected to high static pressures in DACs have been acquired to study terrestrial mantle properties (Daniel et al. 1995, 1997; Farber and Williams 1996; Kubicki et al. 1992). The largest Raman peak, 503 cm^{-1} in anorthite, corresponds to symmetric stretching motions of oxygen atom along the line bisecting the T–O–T line (Daniel et al. 1997; Freeman et al. 2008). Daniel et al. (1997) showed that above 10 GPa, the 503 cm^{-1} peak merged with the 513 cm^{-1} peak. Around the same pressure, the peak shift with pressure was less, corresponding to $\sim 1.51\text{ cm}^{-1}\text{ GPa}^{-1}$. Between 14.1 and 15.4 GPa, Raman active Si–O–Al bending and stretching modes broadened, indicating deformation of Si and Al tetrahedral bonds (Daniel et al. 1997). There was also a decrease in the peak intensity of all bands. All anorthite peaks disappeared between 15.4 and 16.0 GPa. Amorphous anorthite Raman spectra contained broad bands in the Si–O–Al stretching region from 900 to 1300 cm^{-1} (Daniel et al. 1997).

Recovered experimentally shocked samples also show changes in their Raman spectra in response to shock (Heymann and Hörz 1990; Jaret et al. 2018). Heymann and Hörz (1990) acquired Raman spectra with a 488 nm laser 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 peaks 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). Daniel et al. (1995) noted the appearance of a broad, medium-intensity band around 1000 cm^{-1} in the Raman spectrum of shocked anorthite. This

was similar to the result of Freeman et al. (2008), who presented Raman spectra of a variety of plagioclase feldspars, including a shocked anorthite from lunar meteorite NWA 773 that showed broadening of bandwidths with pressure, consistent with partial conversion to maskelynite. Fritz et al. (2005) used Raman measurements to quantify shock effects in meteorites through detailed analyses of maskelynite. They demonstrated that the progression in shock pressures, as indicated by refractive index changes, can be matched to characteristic degradation of the Raman spectra. However, they did not measure materials subjected to shock pressures lower than those required for maskelynite formation, and they did not correlate their measurements to petrographic textures, but only to refractive index.

Experiments and methods

We conducted a series of experiments focused first on andesine, supplemented with experiments on albite, to test the stability field of amorphous plagioclase and its ability to become a memory glass. Specifically, we consider pressure, time, and strain rate. We apply non-traditional experimental techniques to amorphization in plagioclase. We used two samples. The albitite sample (97–99% Ab₉₈ with minor amounts of sericite, quartz, potassium feldspar, and amphibole) originated from Szklary (Lower Silesia), Poland (Muszynski and Natkaniec-Nowak 1992). The andesine sample (95% An₃₆₋₄₆) originated from St. Urbain province, Quebec, Canada, (STU06-1688). It contained minor amounts of quartz and potassium feldspar (Owens and Dymek 2001). See Johnson et al. (2002; 2003) and Johnson (2012) for sample details.

Micro-Raman analyses

All micro-Raman measurements were completed at the Center for Planetary Exploration (CPEX) at Stony Brook University. Spectra were acquired using a WiTec alpha300R confocal imaging system using a 532 nm Nd YAG laser with 2.24 mW nominal power and a 50X (NA = 0.5) long working distance objective with a spot size of 763 nm. Multiple spots on the sample were examined, and representative spectra are presented. Each Raman analysis consisted of 240 summed 1 s accumulations.

DAC experimental setup

We collected in situ Raman spectra (100–1200 Δcm^{-1}) on a plagioclase single crystal in a DAC as the grain was incrementally and statically compressed and then decompressed through a series of pressures. The diamonds had culet sizes of 450 μm . Single grains of plagioclase (approx.

40 $\times$ 40 μm) were taken from each starting sample. Pseudo-hydrostaticity on the sample was maintained by placing the sample between layers of pre-compressed NaCl (Klotz et al. 2009). The surrounding volume was then filled with additional NaCl, which does not occlude or interfere with the Raman signal from the sample. We chose NaCl as a medium due to its low yield stress (Duffy 2007). NaCl is incapable of supporting high differential stresses (< 2.5 GPa maximum), and therefore limits shear forces. Several rubies were added to measure pressure using the ruby fluorescence technique (Dewaele et al. 2008; Mao et al. 1986) which generally has errors of ~0.2–0.3 GPa. The average of multiple ruby measurements was used when available.

Experimental series

Two samples were used in a total of eight compression experiments. The initial spectroscopic patterns are shown in Figs. 3 and 4 from 1.0 GPa to demonstrate the background behavior for spectra taken through the diamonds at low pressure. Whenever possible, we verified that the samples remained amorphous by using the Raman instrument to examine the grains after decompression with the upper diamond removed. Experiment 1 consisted of stepwise compression and decompression of andesine. Andesine was compressed to 17.9 GPa in a stepwise fashion, stopping at 0.6 GPa, 1.0 GPa, 5.2 GPa, 6.4 GPa, 7.5 GPa, 8.2 GPa, 9.5 GPa, 10.1 GPa, 12.1 GPa, 14.9 GPa, and 17.9 GPa. Raman spectra were acquired at each pressure. After sitting at 17.9 GPa for 5 min, the sample was then decompressed in a series of steps stopping at 15.6 GPa, 11.0 GPa, 9.3 GPa, 6.7 GPa, 2.8 GPa, and 0.6 GPa, with Raman spectra acquired at each pressure. In Experiment 2, andesine was compressed to 18.1 GPa, stopping at 1.9 GPa, 8.1 GPa, 10.2 GPa, 13.5 GPa, 15.8 GPa, and 18.1 GPa. Raman spectra were acquired at each pressure. The sample was then kept in the DAC at 18.1 GPa for 59 days before quenching. Here, we use the term quench to indicate decompression from high pressure to ambient in one step, and does not involve or refer to temperature, melting, or any liquid phases.

Experiment 3 involved quenching andesine directly from a peak pressure of 18 GPa. Andesine was compressed almost directly to 18 GPa and then quenched immediately. No sample measurements were acquired during compression. Pressure increase was paused only long enough to determine the pressure on the sample. Sample spectra were acquired prior to compression and post-quench. Experiment 4 was similar to Experiment 3 and involved quenching andesine directly from 20.3 GPa. The quench and spectral acquisition occurred similarly.

Experiment 5 involved dropping a DAC approximately 1 m, which we hereafter refer to as DAC-drop. To test the effects of rapid pressure increases once at high pressure,

andesine was compressed to 17.7 GPa. Then, the entire cell was dropped onto a plastic table from 1 m height. The cell was dropped carefully to ensure that it landed parallel to the compression axis of the diamonds. Sample spectra were acquired pre-drop and post-quench. During Experiment 6, andesine was compressed to 18 GPa and then the DAC was struck with a wooden mallet. A metal plate was placed on top of the cell prior to striking to ensure that pressure was applied uniformly and that the strike was parallel to the compression axis of the diamonds (see supplementary video file). Sample spectra were acquired after pre-compression, at 18 GPa, and post-quench.

The final experiment was conducted on albite and utilized a methodology similar to Experiments 1 and 2, for which Raman spectra were acquired at every pressure step. Experiment 7 consisted of compressing albite to 39 GPa, stopping at 12 GPa, 14.6 GPa, 27.4 GPa and 39.9 GPa. It was then quenched immediately.

Spectral processing

Raman spectra were not corrected for background fluorescence. Several locations on each sample were examined to verify the uniformity of deformation and the spectra shown are representative. Pressure steps were not uniform due to the difficulty of estimating pressure during manual pressure change. The peak at 305 Δcm^{-1} in each spectrum is an artifact produced by a hot pixel on the detector.

Results

Prior to compression during Experiment 1, andesine exhibited micro-Raman spectra with characteristic peaks at 287, ~480, and 510 Δcm^{-1} with additional peaks near 410 and 571 Δcm^{-1} (Fig. 1a). With increasing pressure, two distinct changes occurred to the spectra: (i) all peaks shifted to higher wavenumbers and (ii) all peaks decreased in intensity, most notably the 480 and 510 Δcm^{-1} peaks, which were completely lost by 14.9 GPa. The peaks at 480 and 510 Δcm^{-1} merged into a single peak centered at 527 Δcm^{-1} at pressures above 5.2 GPa. McKeown (2005) indicates that these features correspond to Group I stretching modes and ring breathing modes. Group III modes broadened above 7.5 GPa. Up to 10 GPa, there was a decrease in peak intensity, an increase in the peak ratio of the 485–514 Δcm^{-1} peaks, and a migration of all peaks to higher wavenumbers. The Group III modes disappeared at 12.0 GPa. As indicated by the total absence of peaks, amorphization occurred between 12 and 18 GPa. On decompression (Fig. 1b), the sample reverted to a more crystalline form. The peak intensities of the fully decompressed spectrum were lower than the pre-compression sample. However, the 485/514 Δcm^{-1} peak ratios were identical to within the error of the measurement. The peaks in the recovered sample were not broadened compared to the original sample.

For Experiment 2, the sample showed a systematic progression of decreasing peak intensities (Fig. 2a) during progressive compression. All peak positions shifted to higher wavenumbers with increasing pressure. At 18.1 GPa, only a broad weak peak at ~580 Δcm^{-1} was evident, with no peak intensity from the other peaks remaining. The sample remained at peak pressure for 2 months, during which the

Fig. 1 **a** Stacked profile of Raman spectra for andesine sample during compression to peak pressure of 17.9 GPa. **b** Stacked profile of Raman spectra for andesine sample during decompression from 15.6 GPa

Fig. 2 Stacked profile of Raman spectra for andesine sample left at pressure for 59 days. **a** Measured pressures appear above each spectrum. The last pressure increase to 18.2 GPa occurred on August 28,

2016. **b** The pressure and date of each measurement appear above the spectrum. The 310 Δcm^{-1} band is an artifact

pressure increased slightly to 18.2 GPa (within uncertainty of the measurement). After 59 days, on August 28, 2016, the Raman spectrum appeared to be nearly identical to the Raman spectrum acquired immediately after reaching high pressure (Fig. 2a). After quenching, the peaks did not reappear. The sample was monitored for 12 days after decompression, during which no change was observed.

In the third experiment, andesine was compressed to 18.0 GPa. The compression was followed by immediate quenching. After quenching, the sample exhibited weak peaks at 507 and 478 Δcm^{-1} (Fig. 3). In Experiment 4, andesine was compressed to a peak pressure of ~ 20.3 in the same manner as Experiment 3. The sample was immediately quenched after pressure measurement. After quenching, the sample did not show any crystalline peaks (Fig. 4b). However, a weak broad peak near 580 Δcm^{-1} was observed. The spectra of the quenched samples from Experiments 3 and 4 are compared in Fig. 5.

In Experiment 5, a DAC loaded with andesine was dropped from a height of 1 m. The cell was pre-pressurized as quickly as possible to a pressure of 17.7 GPa. The spectrum acquired at 17.7 GPa is shown in Fig. 6b. Only a broad peak near 550 Δcm^{-1} was present. After performing the DAC-drop from a height of 1 m, the spectra measured while still under compression remained mostly amorphous, indicating no change to the sample spectrum. After quenching (Fig. 6c), the sample appeared to have somewhat recrystallized, showing a weak peak at 512 Δcm^{-1} .

For Experiment 6, the andesine sample was compressed as quickly as possible to a peak pressure of 18.0 GPa. A spectrum was acquired at 18.0 GPa, and the sample was found to be amorphous (Fig. 7b). After hitting the cell with the mallet (see supplementary video), the cell reached an estimated peak pressure of 36 GPa as verified using ruby fluorescence. The sample was checked to ensure it was

Fig. 3 Spectra of andesine quenched from 18.0 GPa. **a** A typical low-pressure spectrum. **b** Spectrum of the post-quench sample

Fig. 4 Spectra of andesine quenched from 20.31 GPa. **a** A typical low-pressure spectrum. **b** A spectrum from the post-quench sample

amorphous, but in the interest of keeping the residence time as short as possible, no full spectrum from the sample was taken at peak pressure. The post-quench spectra indicated the presence of an amorphous material, with broad peaks near 580, 760, and 1020 Δcm^{-1} (Fig. 7c), although crystalline peaks did not reappear (Fig. 7c).

Fig. 5 **a** Spectra of andesine sample quenched from 18.0 GPa (Fig. 3b). **b** Quenched from 20.3 GPa (Fig. 4b)

Fig. 6 Raman spectra of andesine from the DAC drop experiment. **a** A typical low-pressure spectrum before the DAC was compressed and dropped. **b** Spectrum acquired at a pressure of 17.7 GPa prior to the drop. **c** Spectrum acquired after sample decompression

Fig. 7 Raman spectra of sample from SMACA-DAC experiment. **a** The andesine sample prior to the experiment. **b** A spectrum from 18.0 GPa. No sample measurements were taken at 36 GPa, while the sample was amorphous. **c** A spectrum from sample post-quench

Experiment 7 utilized an albite sample to examine the effect of Na content. Initially, albite micro-Raman spectra contained characteristic peaks at ~ 291 , ~ 479 , and 507 cm^{-1} at 0.0 GPa (Fig. 8). As pressures were increased to 12.0 GPa, the 479 and 507 cm^{-1} peaks merged. The sample became fully amorphous between 27.4 GPa and 39.9 GPa. The spectrum from the decompressed sample contained no resolvable peaks.

Fig. 8 Stacked profile of Raman spectra for albite sample. Measured pressures appears above each spectrum

Discussion and conclusions

Daniel et al. (1997) found that anorthite samples can become amorphous, appear amorphous, and then regain crystallinity on decompression. They observe that this behavior is dependent on the peak pressure attained. In this work, we examine this impermanent amorphization. We also study the conditions for the pressure threshold where plagioclase samples remain amorphous upon decompression.

Memory effects

Prior to compression, feldspar structures contain rings of four and six tetrahedra. The low wavenumber ($\sim 200 \text{ cm}^{-1}$) modes disappeared first upon initial compression. McKeown (2005) identified these features as resulting from four-membered ring and tetrahedral cage shear-rotation displacements. The disruption of the low wavenumber modes indicates the structure has been altered in a way that suppresses those motions, while leaving other features unaffected. The loss of these modes may indicate loss of long range order. Other peaks became more distinct at higher pressure, such as the $571\text{--}830 \text{ cm}^{-1}$. Aliatis et al. (2017) attributes these features to deformation of the tetrahedra. The change may be due to either differences in background fluorescence in that part of the spectrum or simply due to additional deformation. The peaks that disappeared last, between 450 and 520 cm^{-1} , are characteristic of the feldspar structure (Sharma et al. 1983). McKeown (2005) attributes these peaks to ring breathing modes of the four-membered tetrahedra. The retention of these peaks possibly indicates that a subset of comparatively undeformed rings might persist to higher pressures than other structural features that are characteristic of the crystalline structure. Aliatis et al. (2017) suggests that deformation in Si tetrahedra is greater than that in the

Al tetrahedra. In andesine, peaks in the decompressed sample were of lower intensity but were not broadened, which may reflect a variety of deformation mechanisms involving the closing up and partial reopening of the crankshaft unit without involving disruption of this unit, similar to what has been suggested for plagioclase deformation (Aliatis et al. 2017; Angel 1988). The peak shift to higher wavenumbers occurred in all samples, indicating decreases in bonding lengths (Hemley et al. 1986). At high pressure, the data suggest that the ring structures were altered such that relevant breathing modes no longer appeared. A nuclear magnetic resonance spectroscopic study by Jaret et al. (2015) suggested that the T–O–T bonding still exists at higher pressures, which our study corroborates.

Andesine appeared to show evidence of pressure-induced memory effects, similar to anorthite as measured by Daniel et al. (1997) and Williams and Jeanloz (1989). Andesine compressed to ~18 GPa reverted back to a crystalline phase upon decompression, albeit with less pronounced spectral peaks than the initial uncompressed sample. This occurred both during stepwise decompression (Fig. 1b) and during immediate quenching (Fig. 3), suggesting that time and kinetics of decompression are not critical to this reversion. However, the peaks from the immediate quench (Fig. 3) experiment were stronger than peaks from the stepwise decompression (Fig. 1b). The reduced intensities may indicate either fewer unaltered structures remain post-experimentation or changes in ring statistics.

Interestingly, the andesine compressed to 20.3 GPa did not revert upon decompression (Fig. 4). This suggests that the atomic displacements induced by compressing to 18 GPa were smaller than those induced by compressing to 20.3 GPa, such that 18 GPa is not sufficient static pressure to cause a complete transformation. The andesine stepwise pressurization experiment (Experiment 1) and the two quench experiments (Experiments 3 and 4) suggest that there may be an energy well around 18 GPa such that an additional energy input is needed to push the system toward a complete transformation. Further, remaining at the critical 18 GPa pressure for 2 months (Fig. 2) was sufficient time for the atoms to arrange themselves in a manner that resists reversion upon decompression. That experiment indicated that time can possibly play as important a role as pressure and strain rate at longer timescales.

To further evaluate this apparent energy well at ~18 GPa, we tested the effect of sudden addition of energy to the system by dropping the loaded DAC parallel to the diamond's compression axis. Dropping the cell from 1 m did not provide enough additional energy to push the system to complete amorphization, as shown in Fig. 6, where the post-drop spectra display crystalline peaks at 510 cm^{-1} . We then tested a greater energy spike—directly striking the DAC with a wooden mallet. This was a large enough spike to

induce a complete transformation, as shown in Fig. 7. After hitting the cell and subsequently quenching, only a broad peak remained, and the andesine did not revert. Based on the position of ruby fluorescence peaks, we estimate that hitting the cell nearly doubled the pressure from 18 to 36 GPa. The diamond anvils were not damaged during the experiment.

This set of non-traditional DAC experiments show that around 18 GPa (at 25 °C) the system is metastable such that it requires an additional ‘kick’ to push it over the threshold for complete transformation. This ‘kick’ is either a change in max P (Experiment 4 and the hammer Experiment 6), more time (Experiment 2), or passage of an acoustic wave through the sample. More so, we show that in the case of passing an acoustic wave through the sample, it requires a significant (although admittedly not quantified) wave. The energy imparted from dropping the DAC from 1 m was not enough to push the system toward complete amorphization, but hitting it with a hammer was. This shows that the system is metastable with respect to multiple variables beyond the standard P and T most commonly discussed.

Amorphization pressures in andesine

In plagioclase samples, the pressures at which amorphization begins and completes is dependent on a number of variables, including hydrostaticity (deviatoric stress), temperature and compression rate (Daniel et al. 1997; Sims et al. 2019; Tomioka et al. 2010). Deviatoric stress has an effect on amorphization pressures in our samples. In anorthite, Daniel et al. (1997) observed that amorphization initiation and completion pressures were reduced under less hydrostatic conditions. With NaCl as a medium, deviatoric stress in the diamond anvil cell reaches 2 GPa at enclosure pressures of 5 GPa (Reynard et al. 2019). The deviatoric stress eventually reaches 2.5 GPa at 7 GPa pressure, and it remains at that value up to 20 GPa (Reynard et al. 2019). In andesine, we observe that amorphization begins below 5.3 GPa and is complete by 12 GPa. Therefore, both amorphization initiation and completion in andesine are affected by deviatoric stresses of at least 2 GPa. Amorphization pressures in andesine might be higher in other mediums. In albite, the effect of deviatoric stress is less obvious. With no pressure medium, Tomioka et al. (2010) found amorphization in albite was complete by 37 GPa. We found albite to amorphize between 27 and 39 GPa.

Based on the experiments in this study, we infer that amorphization of andesine is displayed in two ways. In the first mode, the sample begins to become amorphous when measured under compression. We interpret this to be the same “amorphization initiation” point that Daniel et al. (1997) described for anorthite under static conditions. The second mode is at higher pressure at which amorphization is complete, such that the sample will remain amorphous

after decompression. For andesine that did not remain at high pressure for long periods, we observed an initiation of amorphization around 18 GPa, whereas amorphization was complete around 21 GPa. These values are higher than those reported for anorthite by Daniel et al. (1997), but this is expected because of known compositional effects on amorphization point in feldspars (e.g., Kubo et al. 2010). For example, in prior DAC and shock experiments (Daniel et al. 1997; Redfern 1996), more calcic feldspars transformed at lower pressures. While this has been described in terms of Ca content previously, it likely is not related to the calcium itself, but rather by the subsequent Al bonding changes that result from the coupled substitution in plagioclase. Amorphization typically involves changes in the Si–O tetrahedral Si-polymerization, and therefore changing the Al–Si ratio will change the ordering in the feldspars. The more calcic (or more Al rich) plagioclase may not have the same bonding capability as a more sodic (with more Si–O tetrahedra) plagioclase.

Generally, the different plagioclase compositions had similar behavior with increasing pressure. The peaks shifted to higher wavenumbers with increasing pressure, indicating reduction in size of the rings of tetrahedra. The peaks broadened and intensity decreased, indicating a variety of local environments and fewer Raman active vibrational modes. The last sharp features to be lost were the 560 cm^{-1} peak and the largest peak, 520 cm^{-1} here. Based on work by McKeown (2005) and Freeman et al. (2008), these features can be attributed to Group V deformation modes and Group I s bending deformation of the T–O–T bonds. The changes indicate structure has been altered in a way that suppresses that motion.

We mainly focused on andesine because previous work focused on nearly pure-Ca endmember compositions where memory effects were noted (Daniel et al. 1997), but other transformations in plagioclase (particularly transformation to the high-pressure polymorph tissantite (Ma et al. 2014; Rucks et al. 2018) seem to require intermediate compositions. Therefore, our experiments are supplemented with work on albite, in which we observed amorphization at significantly lower pressures (27.4–39.9 GPa) than is found in shock experiments (50–56 GPa; Jaret et al. 2016; Johnson and Hörz 2003).

Implication for pressure barometry of natural samples

The memory effect seen in these experiments presents some complications for barometric studies of natural materials—particularly shocked rocks. The influence of temperature on the memory effect is not clear. For studies of naturally shocked materials, measurements are conducted on samples that have been fully decompressed, and Raman

spectra, particularly peak intensity ratios, are used to assign a pressure estimate (e.g., Fritz et al. 2005). We demonstrate that amorphization is affected by the length of time at peak pressure as well as the peak pressure reached and the time required to reach the said peak pressure. When a sufficiently high pressure is reached, the memory effect is lost. However, we show that crystalline peaks partially return for samples below the amorphization completion point when subjected to static pressures. While further experiments would be useful, the DAC strike and DAC drop experiments suggest the effect may occur in shock experiments with peak pressures below 36 GPa, but experiencing a high strain rate during compression. Bearing in mind the differences between static compression and natural impacts, it may therefore be very difficult to distinguish between samples that were compressed to low peak pressures from those that have actually seen higher pressures but have reverted. In this case, the actual peak pressures seen would not be known as the post-decompression measurements would be recording the reverted crystalline structure and therefore one could drastically underestimate the actual peak pressures seen in these materials during shock compression (Fig. 3). This may also partially explain some of the discrepancy in “amorphization pressure” observed between static in situ and shock experiments. Shock experiments typically indicate higher amorphization P than static compression, but this may be reflecting the ultimate max P for amorphization completion rather than the initial amorphization onset observed by in situ measurements.

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