

Raman-Spectroscopy and X-Ray Diffractometer Studies of Experimentally Produced Diaplectic Feldspar Glass

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Abstract. Raman vibrational spectra and X-ray diffractometer scans were obtained from experimentally shocked samples of oligoclase (An₁₉) and andesine (An₄₉). Some 11 oligoclase and 15 andesine targets were shocked between 24 and 40 GPa to address the transition from crystalline to diaplectic states and to explore differences in the structural state of diaplectic feldspar glasses (maskelynite) as a function of peak shock stress. The symmetrical VS (T–O–T) (T=Si or Al) stretch bands are the most persistent. They disappear, however, in the noise of an unusually strong luminescent spectrum at >32 GPa in the oligoclase and at >30 GPa in the andesine; i.e., at pressures where transition to diaplectic glass is complete. The Raman investigations yield a maskelynite structure that is probably one of a multitude of very small domains with some order, but with a large range of local properties on the scale of small domains, either in heterogeneous size-distribution of domains or in their detailed order, if not both. This results in a very large number of Raman photon-phonon frequencies unlike glasses derived from quenched melts. Our study corroborates conclusions by others, that diaplectic glasses may be the quench products of very dense, disordered phases that exist during shock compression and that subsequently relax to these unusually dense glasses that are only known from shock processes. An origin by relaxation of highly ordered, genuine high pressure polymorphs possessing the structure of hollandite is unlikely, as no evidence for any six-fold Si-coordination was found. Detailed luminescent emission spectra were taken of the oligoclase samples and they show disappearance of the IR band and a strengthening of the green band (the blue band could not be detected with a primary radiation of wavelength 448 nm). This supports previous views that the disappearance of IR emission is most likely caused by shock-induced changes of the crystal field near Fe³⁺ sites, rather than due to quenching by Fe²⁺. The X-ray studies were primarily intended to explore whether differences in structural states of maskelynite occur on sufficiently large scales to be detected by standard diffractometry methods. This is not the case. X-ray diffractometer patterns are grossly similar, if not identical, in samples shocked between 30 and 40 GPa and may not be used to fine-tune the shock histories of naturally produced diaplectic glasses.

Introduction

The irreversible changes in the structural states of silicates that were shocked beyond their Hugoniot Elastic Limit are of interest in their own right, but they may also illuminate details of a sample's natural shock history. Such changes refer to the mechanical disaggregation of a crystal's long- and short-range order, to the deformation of unit cells, to the generation of high-pressure polymorphs, to changes in valence states and to next-neighboring lattice configurations and arrangements of SiO₄ tetrahedra. Many of these changes are sensitively related to peak shock stress, thereby providing the means to extract specific shock histories from rocks and minerals subjected to natural impact processes (French and Short 1968; Stöffler 1972, 1974). Of specific interest towards an understanding of extraterrestrial materials and associated planetary surface processes is the shock behavior of feldspar.

Tschermak (1872) has discovered in the Shergotty achondrite an isotropic form of plagioclase that he termed "maskelynite". Such phases preserve in great detail the habits of the crystalline progenitors; the conspicuous lack of flow features and vesiculation suggests a solid state phase transition. Their origin by shock was demonstrated by Milton and DeCarli (1963). Maskelynite is now considered as a specific form of "diaplectic" glass (Engelhardt and Stöffler 1968) and as a diagnostic indicator for impact processes.

A recent review by Stöffler (1984) summarizes the differences between such diaplectic glasses and bona fide impact melts. Texturally, genuine shock melts are distinguished from maskelynite by the presence of flow features and vesiculation. However, the more substantive differences are structural, as revealed first by refractive index measurements (Bunch et al. 1967, 1968; Duke 1968; Dworak 1969; Stöffler and Hornemann 1972; Gibbons and Ahrens 1977; Ostertag 1983; Lambert and Grieve 1984; Stöffler et al. 1986). Ostertag (1983) summarizes infrared absorption properties of experimentally shocked feldspars and finds line-broadening and associated loss of fine structure systematically correlated with peak shock stress; Stöffler and Hornemann (1972); Gibbons and Ahrens (1977), and Arndt et al. (1982) produced similar results and conclusions. X-ray

diffraction work (Hörz and Quaide 1973; Hanss et al. 1977; Dieman and Arndt 1984), crystallization experiments and other comparisons to either genuine melts or to ideal single crystals (Arndt et al. 1982) were performed subsequently. Also, Grady (1980) developed some thermodynamic framework for phase transitions during shock that was applied by Arndt and co-workers to diaplectic feldspar glasses. Accordingly, diaplectic glasses such as maskelynite, may represent the relaxed recovery products of very dense, disordered states produced during shock compression that had strong structural affinities to very dense melts.

The infrared results suggest strongly that the transitions from crystalline to noncrystalline states must be observable in Raman vibrational spectra also. Velde and Boyer (1986) have done Raman spectroscopy and X-ray diffraction studies on single crystal albite and anorthite from a few shock experiments in the pressure range 20–40 GPa. The albite Raman spectrum at 21 GPa is still essentially the same as that of the unshocked albite, but the 39 GPa specimen displays considerable broadening and weakening of Raman lines and is very similar to the Raman spectra of thermal melts that were quenched while at confined pressures. The anorthite spectra show even stronger effects of line broadening.

The X-ray results of Velde and Boyer (1986) are consistent with previous findings and reveal X-ray amorphous materials for shock stresses > 30 GPa, consistent with Hörz and Quaide (1973) and Hanss et al. (1977) and Ostertag (1983). Accordingly progressive mechanical breakdown of the feldspar lattice occurs with increasing shock stress, resulting in ever decreasing domain sizes that ultimately are beyond coherent X-ray diffraction. This transition occurs at approximately 30 GPa for feldspars, but is modestly dependent on composition (Ostertag 1983).

The objective of this study was to learn more about the processes of transformation from crystalline to diaplectic states of plagioclase and about the structural states of diaplectic glasses within their known stability field of approximately 30 to 40 GPa. Of specific interest was the question, whether phenomena and changes occur that are sensitively related to peak stress, such that fine-tuning of the pressure history for naturally produced maskelynite may be accomplished. Progressive structural changes may be postulated between 30 and 40 GPa based on the behavior of the refractive index. While n drops dramatically during the initial phase-transition for crystalline to diaplectic states, it nevertheless continues to decrease between 30 and 40 GPa to asymptotically approach the values of the true glasses (=quenched melts) at > 40 GPa (Ostertag 1983; Lambert and Grieve 1984). Also, the X-ray diffraction studies of Hanss et al. (1977) provide qualitative indications that changes in structural states may be reflected in modest changes of the X-ray diffraction spectra at pressures > 30 GPa. Because this study focuses on diaplectic states, the samples were shocked in very small pressure increments, typically < 2 GPa, covering the crystalline/diaplectic phase transition (25–30 GPa) and the maskelynite stability field (30–40 GPa).

Experimental Conditions

Sample Selection

Single crystal feldspars were employed as target materials for the shock recovery experiments. The oligoclase was

from Muscwa Lake, Ontario, and the andesine from the Harvard University collection, terrestrial locality undocumented. Both materials were almost translucent and free of macroscopic defects, fractures, accessories, or secondary minerals. The Muscwa Lake oligoclase (An_{19}) was part of a previous X-ray study by Hanss et al. (1977) and Ostertag (1983). The An_{49} andesine was purposely selected as an analog to Shergotty meteorite feldspars. The shock history of these meteoritic maskelynites is presently the subject of lively and important debate related to the reputed Martian origin of SNC meteorites (Lambert and Grieve 1984; Lal 1986; Stöffler et al. 1986).

Shock Experiments

The cm-sized single crystal feldspars were cored, wafered and polished into discs of some 5 mm diameter and 0.5 mm thickness, before being placed into metal sample holders for the actual shock experiments (see Gibbons and Ahrens 1977). The latter were carried out using a 20 mm powder-propellant ballistic range (see Hörz 1970). The velocity of the flat-plate projectile was measured to within 1% and the peak-pressure was solved via graphical impedance match methods (Duvall and Fowles 1963), using equations of state for the appropriate target and flat-plate impactor metals (Marsh 1980), such as aluminium, stainless steel and tungsten. X-ray flash tubes monitored the planarity

Table 1. Experimental conditions of shock recovery experiments for materials analyzed in this study

	Shock Pressure (GPa)	Impact Vel. (km/s)	Flyer Plate	Sample Holder
Oligoclase (Muscwa Lake)				
a	unshocked starting material			
b	24.7	1.829	Al*	99*
c	26.3	1.208	SS	SS
d	28.0	1.277	SS	SS
e	30.0	1.352	SS	SS
f	30.9	1.352	SS	SS
g	32.4	1.445	SS	SS
h	36.9	1.609	SS	SS
i	39.9	1.722	SS	SS
j	43.1	1.399	W*	SS
k	49.1	1.569	W	SS
Andesine (Harvard)				
a	unshocked starting material			
b	24.5	1.524	Al	FS*
c	24.9	1.533	Al	FS
d	26.9	1.234	SS	SS
e	27.8	1.253	SS	SS
f	29.4	1.320	SS	SS
g	30.5	1.372	SS	SS
h	31.1	1.395	SS	SS
i	32.8	1.462	SS	SS
j	33.8	1.497	SS	SS
k	34.5	1.521	SS	SS
l	36.6	1.597	SS	SS
m	38.2	1.658	SS	SS
n	39.3	1.700	SS	SS

* = Flyer plate or sample holder metals of known equations-of-state (Marsh 1980): Al = Al 2024 T4; SS = stainless steel 304; W = tungsten (> 99% W); FS = "Fan Steel" (trade name); alloy of (> 90% W).

of flyer-plate position to insure a plane shock geometry in the feldspar target. The detailed experimental conditions listed in Table 1 lead to a pressure accuracy of <3% for final equilibration pressure after multiple reverberations (see Tyburzy and Ahrens 1986).

The shocked samples were recovered from their metal jackets via a combination of careful machining on the lathe until the shocked targets were visually exposed. They were then manually pried and dislodged from the target container via dental tools, etc. These procedures commonly yield coherent grains several mm² in surface area. Such "large" fragments were used for the Raman spectroscopy work. The remainder of the target (some 20–30 mg) was carefully ground to <63 μm grain size and used in the X-ray investigations.

X-Ray Diffractometry

The ground samples were carefully weighed and 5% of CaO was added as an internal standard. This mixture was suspended in alcohol to make a slurry which in turn was allowed to control homogeneous sample distribution and thickness (=constant diffraction volume) on the sample carrier glass-slide.

A variety of scan-conditions were explored (count rates, goniometer scan speed, etc.) to yield optimum patterns at consistent diffractometer settings where possible, especially for maskelynite-grade materials. Unfortunately, final X-ray patterns could only be obtained some seven months after initial addition of the CaO standard, because of persistent X-ray equipment problems; this caused the CaO to deteriorate to various degrees, limiting its utility as an internal standard without affecting, however, the general conclusions reached below.

Raman Spectroscopy

The source of the primary radiation at wavelength 488 nm was a Spectra Physics Ar⁺ ion laser. After the filtering out of the plasma lines, the beam was focused with a small telescope to a diameter of approximately 0.5 mm on the surface of the samples. For most measurements, the power at the sample's surface was near 80 mW. Occasionally, measurements were done with power near 100 mW. Most samples were measured at least once in the range 200–1200 cm⁻¹ delta wavenumber with steps of 1 cm⁻¹. Several oligoclase samples were measured in the range 450–550 cm⁻¹ with steps of 0.5 cm⁻¹. Several andesine samples were measured for 200–700 cm⁻¹ or from 400–1000 cm⁻¹.

The samples were mounted on a vertical holder, which could be moved in three orthogonal directions to focus the scattered light onto the entrance slit of a SPEX 1403 Ramalog double spectrometer. The scattered light was collected at an angle of 60° with regard to the incident light. All samples were cleaned with hexane prior to each measurement.

We always opened the entrance slits with the spectrometer set at 1300 cm⁻¹ delta wavenumber. The counting rates at this shift value, where no plagioclase Raman line occurs, would be huge, typically near 10⁴ counts per second for the unshocked samples, but 10⁵–10⁶ c.p.s. for the shocked samples. The counting rates would always decrease, but eventually level off. Our standard procedure was, therefore, to wait at least ten minutes before Raman data were stored.

The delta wave-length shifts of the SPEX 1403 spectrometer were calibrated with HOPG (Highly Ordered Pyrolytic Graphite).

Luminescent Emission Spectra

These were obtained in essentially the same manner as the Raman spectra, except that the wavelength ranges were much longer, i.e., up to 200–9000 cm⁻¹ delta wavenumbers. Spectra were taken with 10 cm⁻¹ increments. Given the 488 nm wavelength of the primary radiation, this range corresponds to an absolute wavelength range of 493 to 870 nm.

Results

X-Ray Investigations

The X-ray diffractometer scans are illustrated in Fig. 1; only data related to feldspar are shown, and the internal

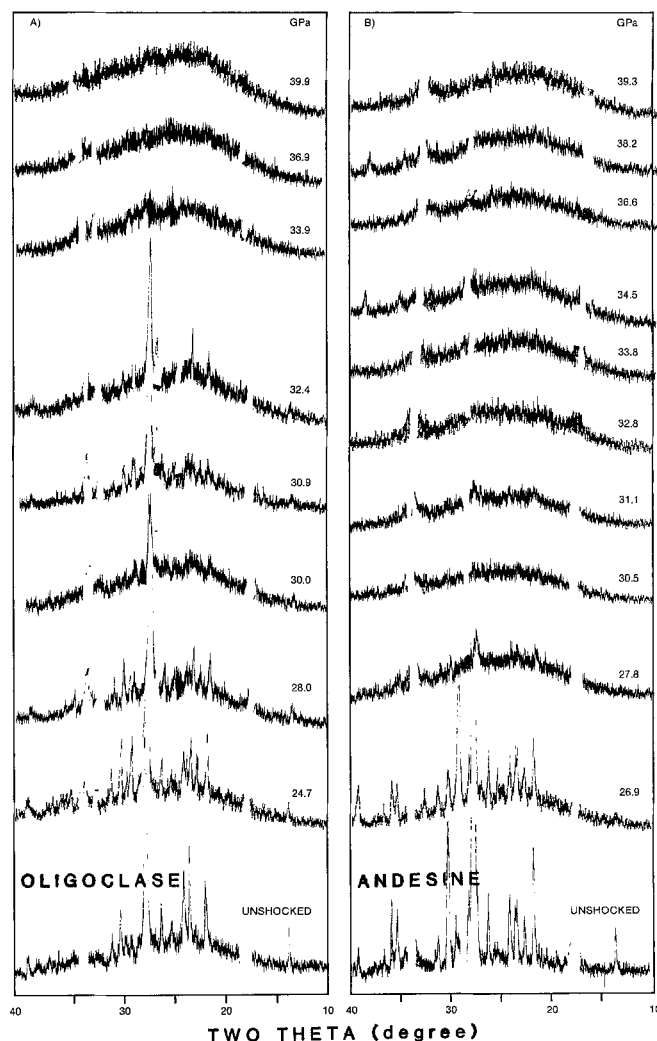


Fig. 1A and B. Representative X-ray diffractometer patterns of experimentally shocked oligoclase (An₁₉, A) and andesine (An₄₉, B). Note that some short-range order is preserved in oligoclase up to approximately 33–34 GPa, while andesine turns completely X-ray amorphous at some 27–28 GPa. Also, none of the major features characterizing the dominant "glass" hump, such as peak height or degree of line broadening, changes substantially and in systematic fashion throughout the stability fields of diaplectic glass. The oligoclase sample at 39.3 GPa represents quenched melts

CaO standard or its secondary products (carbonate; hydrated species) were deleted for clarity. Consistent with previous X-ray studies, especially the diffractometer scans of Hanss et al. (1977), the transition between crystalline and X-ray amorphous states occurs over a narrow pressure interval. Oligoclase seems to be substantially more resistant than andesine. Over the short-range order investigated (2 theta 10 to 40°), oligoclase displays substantially more order up to some 33 GPa than does andesine, which is essentially X-ray amorphous already at 28 GPa. Vestiges of major, coherently diffracting lattice planes persist in oligoclase up to some 33 GPa, but have disappeared by 34 GPa.

These findings seem consistent with the optical studies of Ostertag (1983) who observed complete transition to diaplectic glass at some 32–33 GPa in the case of the same Muscwa Lake oligoclase, but at some 28 GPa for a labradorite of An₆₅. Also, substantially more absolute changes in the refractive index occur in the pressure range 28–39 GPa (specifically between 30 and 35 GPa) in oligoclase as opposed to high Ca-plagioclase (Figs. 4 and 5 of Ostertag, 1983).

Somewhat gradual changes over some modest pressure range are to be expected for the modestly more open oligoclase structure compared to plagioclase of >An₅₀. However, we do not understand in detail why Ca-rich, and thus more stable lattice (e.g., Smith 1974), undergo complete isotropization at lower shock stresses than alkali-rich plagioclases. Nevertheless, these empirical observations characterize all structural investigations, including Ostertag's detailed Infrared and Electron Paramagnetic Resonance studies and our own Raman spectra (see below).

The gradual structural changes in, e.g., refractive index or IR-properties throughout the stability field of diaplectic feldspar glass – albeit far from being linearly related to pressure – precipitated in part the present X-ray studies. As indicated by Hörz et al. (1986), it was hoped to derive some means of relatively rapid pressure calibration for naturally shocked plagioclases from detailed shape analysis of the X-ray scans, specifically the broad “glass” hump between some 15 to 35° 2θ. Visual inspection of Fig. 1 reveals little change in fine-structure of these X-ray patterns, however. Therefore, no quantitative shape analyses were performed, because even modest recovery and incipient recrystallization, a process of high probability in naturally shocked samples, could rapidly modify if not dominate such shape differences, which are very subtle, at best, to begin with.

Thus, standard X-ray diffractometer scans are not useful in fine-tuning the pressure history of natural diaplectic feldspar glasses. The method simply verifies that domain sizes remain sufficiently small to inhibit coherent X-ray diffraction over the entire stability field of diaplectic glasses.

Raman Spectra

1. Oligoclase. Figure 2A presents the vibrational Raman spectra of the oligoclase samples in the range 200–1200 cm⁻¹. The strongest lines in the unshocked sample occur at 505 cm⁻¹ and 475 cm⁻¹. Medium strong lines occur at 288 cm⁻¹ and 1099 cm⁻¹ (which is actually a multiplet in our sample). There are weak lines at 204 cm⁻¹, 284 cm⁻¹, 409 cm⁻¹, 763 cm⁻¹, and 819 cm⁻¹. (Note: the unshocked oligoclase was actually measured on five distinct spots. The five spectra are identical.) With increasing shock

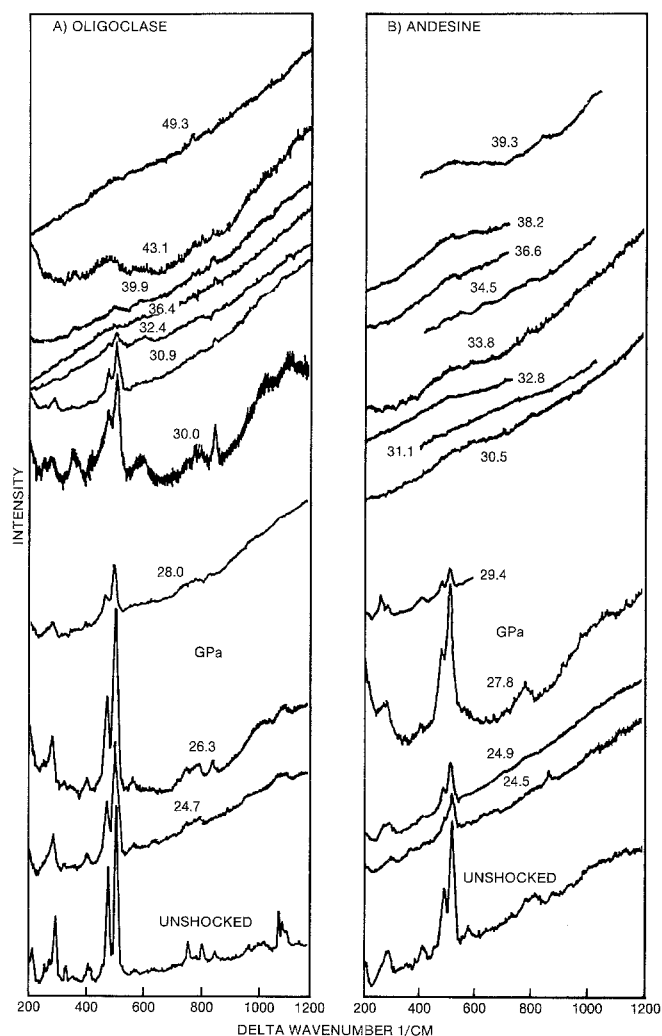


Fig. 2A and B. Vibrational Raman spectra of unshocked and shocked oligoclase (An₁₉, A) and andesine (An₄₉, B). The laser wavelength was 488 nm; the vertical scale is different for each sample, and the heights of bands near 480 cm⁻¹ of the unshocked and modestly shocked samples are higher than those of diaplectic oligoclase and andesine, respectively. Note that oligoclase is somewhat more resistant the shock isotropization than is andesine

pressure, we observe line broadening, decrease of scattering power, and the “disappearance” of lines by being overwhelmed by the luminescence background. The first lines to “disappear” are the shifts at 763 cm⁻¹, 819 cm⁻¹, and 1099 cm⁻¹. The most persistent lines are the ones at 419 cm⁻¹, 476 cm⁻¹, and 505 cm⁻¹, precisely the wavenumber range in which the distinct band structure in the infrared becomes obscured (Ostertag 1983). At 30.0 GPa pressure, the scattering power of the remaining lines has become very weak, and above about 33 GPa, the Raman spectra became essentially featureless. Any Raman scatter which is present in these spectra is masked by the huge luminescent background. Repeat measurements in the range 450–550 cm⁻¹ are consistent with Fig. 2A.

2. Andesine. Figure 2B presents the andesine (An₄₉) Raman spectra. These spectra were more difficult to obtain than the An₁₉ spectra, in part because the scattering yields of the andesine were considerably less than of the oligoclase; in part, also, because several of the andesine chips were

very small. When one compares Fig. 2A and 2B, one notices distinct differences between An_{19} and An_{49} . The line near 1100 cm^{-1} is much weaker in the unshocked andesine than it is in the oligoclase, and the lines at 804 cm^{-1} and 763 cm^{-1} are broader and weaker in andesine. These differences are consistent with the trend in the spectra of albite and anorthite reported by Fabel et al. (1972). The lines at 505 cm^{-1} and 476 cm^{-1} are, however, the strongest Raman lines in both samples, with the line at 288 cm^{-1} medium strong. The andesine also shows a weak line at 580 cm^{-1} . As in the case of the oligoclase, the lines at 505 cm^{-1} and 476 cm^{-1} are the most persistent. The andesine spectra become essentially featureless for pressures greater than at 30 GPa, indicating complete transition to diaplectic glass.

3. Line Broadening. Figure 3 is a composite of three "short" oligoclase spectra from 450 cm^{-1} to 550 cm^{-1} , taken with 0.5 cm^{-1} steps. The range includes the two strongest lines at 505 cm^{-1} and 476 cm^{-1} . The results clearly show increased line broadening with increasing shock pressure. For shocks in excess of 28.0 GPa, these lines become very broad and weak.

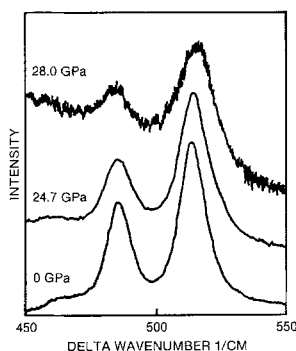


Fig. 3. Broadening of the Raman bands near 480 and 505 cm^{-1} in unshocked andesine and samples shocked to 24.7 and 28.0 GPa, respectively

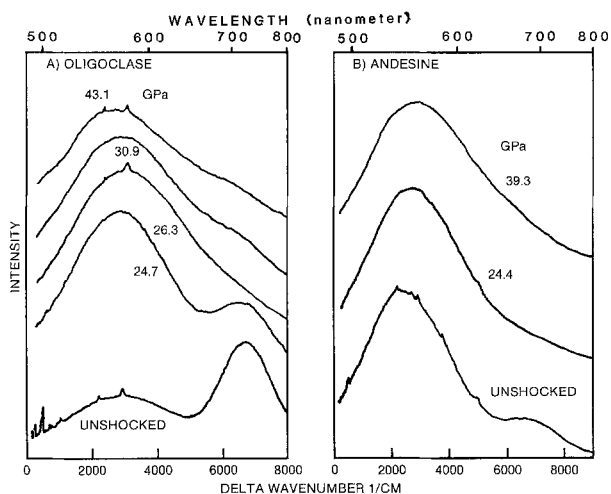


Fig. 4A and B. Luminescent spectra activated with 488 nm laser radiation in unshocked and shocked An_{28} (A) and An_{49} (B) samples. The horizontal coordinate below the figures is the difference, in cm^{-1} , between the absolute wavelength of a photon and the wavelength of the 488 nm radiation. The horizontal coordinate above the figures is the absolute wavelength, in nm, of the luminescent radiation

4. Luminescent Emission Spectra. Figure 4A is a selection from a larger set of "long spectra" of oligoclase. However, the five spectra shown represent well the trend from unshocked to most heavily shocked at 43.1 GPa. The unshocked sample shows two broad bands, centered at about 580 nm and 720 nm absolute, respectively. The number of counts in the two bands is the same within 25%. With increasing shock pressure we observe two phenomena: (a) the 720 nm band becomes increasingly weaker relative to the 580 nm band, and (b) the maximum of the 580 nm band of the shocked samples is from 5- to 10-fold higher than that of the unshocked sample. The 720 nm band becomes undetectable, except for faint "shoulders" (30.9 GPa). The lines "riding" on the fluorescent spectra up to about 516 nm are Raman lines of plagioclase. The lines at larger wavelengths, e.g., near 550 nm and 572 nm, do not occur in all the spectra, hence are probably due to contamination. Figure 4B presents three representative "long spectra" of shocked andesine. When these are compared to spectra of Fig. 4A, we note that the band at 720 nm is much weaker in these samples compared to oligoclase. This 720 nm band is essentially undetectable in all spectra of samples shocked to >24.4 GPa.

Discussion

Several Raman studies of both crystalline as well as amorphous solids of plagioclase composition have been done previously. Most glasses studied were man-made by the melting and congealment (usually quenching) of the constituent oxides. Only Velde and Boyer (1986) have studied shock-produced materials. Raman vibrational data of the crystalline end-members, or, occasionally, near-end-members of the plagioclase have been reported (Fabel et al. 1972; Estep et al. 1972; McMillan et al. 1982; Sharma et al. 1983; Velde and Boyer 1986). All investigators agree that the Raman spectra of crystalline albite and anorthite are very similar. The strongest bands, assigned to VS (T-O-T) (T = Si or Al) symmetrical stretching are near 505 cm^{-1} and 480 cm^{-1} . Symmetrical VS (Si-O-Si) stretch bands occur in the range $1040\text{--}1120\text{ cm}^{-1}$. These bands are, apparently, weaker in anorthite than in albite. Albite has a moderately strong band at 814 cm^{-1} (Fabel et al. 1972), which apparently does not occur in anorthite. Moderately strong bands assigned to "lattice vibrational modes" occur near 250 , 270 , and 280 cm^{-1} . Our observations on unshocked plagioclases are consistent with these earlier studies and reveal little difference between oligoclase and andesine: the strongest bands are near 505 cm^{-1} and 480 cm^{-1} . The bands near 250 , 270 , and 280 cm^{-1} occur in the An_{19} spectrum. The VS (Si-O-Si) bands are weak in the An_{19} and very weak in the An_{49} samples. Our An_{19} sample shows a band at 851 cm^{-1} , which has not been reported before. It may not be a plagioclase Raman line.

Raman spectra of glasses of plagioclase composition formed by the quenching of melts ("synthetic" glasses) usually show distinct, albeit very broad bands at $470\text{--}840\text{ cm}^{-1}$ with broad "shoulders" near about 300 cm^{-1} and 575 cm^{-1} , and weak, very broad bands in the range $900\text{--}1200\text{ cm}^{-1}$; a strong band at 508 cm^{-1} has been reported in a glass of anorthite composition (Sharma et al. 1978; Virgo et al. 1979; McMillan et al. 1982; Sharma et al. 1983, 1985). The spectrum of albite shocked to 39 GPa by Velde and Boyer (1986) shows broad bands near

480 cm^{-1} , 500 cm^{-1} , and in the range 1000–1200 cm^{-1} . Their shock-produced diaplectic glass of anorthite shows broad bands near 500 cm^{-1} and in the range 800–1200 cm^{-1} . All of these bands are “riding” on significant, but not huge luminescent backgrounds. Our results are distinctly different: the An_{10} spectra are essentially featureless for shock pressures >32 GPa; the An_{40} spectra are essentially featureless for pressures >29 GPa. These differences could be real owing to different starting materials and shock-loading conditions. However, they could also be only apparent, because the huge fluorescent backgrounds of our samples could well mask any distinct Raman features present in our spectra. Velde and Boyer (1986) have used a micro-Raman technique, which may be less sensitive to luminescence than ours.

Several studies have concerned themselves with the structural states of diaplectic feldspar glasses that seemingly have affinities to their crystalline precursors as well as their thermally produced, quenched melts. IR studies demonstrate that some distortion and rearrangement of tetrahedra has occurred, signalling the onset of melt formation. Ostertag (1983) specifically interprets diaplectic feldspars and diaplectic feldspar glasses as intimate mixtures of crystalline and melted phases, the volume-fraction of the latter systematically increasing with shock stress. The IR absorption spectra of diaplectic glasses generated at pressures close to shock-induced melt formation are indistinguishable from thermally produced melts, which is Ostertag’s major argument for increasing melt-volumes over a wide pressure range, starting at essentially 15 GPa and reaching completion at some 45 GPa. Arndt et al. (1982) determined a variety of physical properties of naturally shocked, diaplectic labradorite (An_{55}) glass from the Manicouagan Crater, Canada (Dworak 1969), and compared them to similar properties of traditional glasses produced from quenched melts.

Elevated refractive index and densities indicate denser packing for diaplectic glass, yet viscosity and IR-absorption spectra are essentially identical for both glasses (Arndt et al. 1982). The most distinctive difference is in the crystallization behavior: diaplectic glass restores to the original plagioclase grains, totally unlike thermal melts. Arndt et al. (1982) also conclude that crystallization of diaplectic glasses is not diffusion controlled. Relatively small displacements of SiO_4 and AlO_4 tetrahedra that have small numbers of nonbridging oxygens are implied, preserving modestly intact short range order. This manifests itself in some memory-effect of the crystalline progenitor which quenched melts do not have. These unusual structural states are caused by the freezing-in of very dense, disordered states existing during the shock’s compressional phase. The findings and conclusions of Arndt et al. (1982) add to the general debate whether first order constitutive phase transitions, resulting in ordered high pressure phases, occur during shock compression (e.g., Ahrens et al. 1969) or not (e.g., Grady 1980). The structural states of diaplectic glasses seem to be more compatible with Grady’s proposal that envisions very dense, yet disordered structural states during shock-compression akin to very dense melts.

Clearly no evidence for 6-fold Si-coordination, indicating hollandite, was observed in our Raman spectra. When we consider all information at hand regarding Raman effects in solids, we conclude that our samples are characterized by changes in the solid’s phonon structure. These chan-

ges are progressive and related to shock stress that produces increasingly smaller, increasingly more numerous short-range order domains. Such domains, however, have an extraordinarily wide range of dimensions and great variability with regards to internal make-up. If we accept the concept of Arndt et al. (1982) of only comparatively small tetrahedra and major ion displacements, we conclude that there must be great variation among such displacements to cause the progressive line broadening in the Raman spectra. The grain size distribution of relatively large domains that coherently diffract X-rays is highly heterogeneous as well (Hörz and Quaide 1973). Such heterogeneity in domain size and lattice displacements must now be extended to substantially smaller scales approaching unit cell dimensions, if not smaller, as many unit cells must be substantially deformed if not destroyed.

Luminescence is the emission of photons associated with changes in the electronic state of, in this case, solids. In our case, the luminescence occurs in response to the irradiation with the 488 nm radiation, hence the luminescent spectrum cannot contain photon with wavelength shorter than 488 nm. The electronic state of a given solid crystalline or non-crystalline, depends on many factors such as lattice defects, trace element content, or degree of polymerization in the case of glasses.

Terrestrial and lunar plagioclases have long been known to luminesce (see Geake and Walker 1975). Terrestrial plagioclase shows strong bands between about 730 and 780 nm. The main bands of lunar plagioclases, which were at least weakly shocked, are near 450 (blue) and 560 (yellow-green) nm. The blue band is thought to be due to lattice defects. The green band is caused by Mn^{2+} as activator in Ca^{2+} sites (Geake et al. 1971). The near infrared band is thought to be due to Fe^{3+} present as impurity in the plagioclase. Sippel and Spencer (1970) are the only investigators who have reported studies to which ours can be directly compared, with the one distinction that the blue peak present in their spectra does not occur in ours owing to the wavelength of 488 nm of our primary radiation. The spectrum of the An_{85} (terrestrial, crystalline, and unshocked) sample of Sippel and Spencer (1970) is very similar to our unshocked oligoclase and shows two intense bands, one near 680 nm and the other near 560 nm. Crystalline plagioclase from An-rich lunar rocks shows a band near 560 nm plus a blue band near 450 nm; the IR band is absent. A moderately shocked lunar plagioclase grain showed only the green band shifted to 580 nm plus a weak blue “shoulder”. A lunar maskelynite grain showed strong bands near 450 nm and 450 nm.

Our data confirm and strengthen the conclusions of Sippel and Spencer (1970) that the luminescent spectra of shocked plagioclases are characterized by a weakening of the IR band, with the disappearance of this band at increasing shock pressures. We do not reproduce their observation that shock weakens the total luminescent intensity, even in totally isotropic samples. We think that the question which of the bands, green or blue, is most enhanced by shock may depend on many factors, none of which are even marginally understood at this writing.

Geake and Walker (1975) have considered causes for the absence of the IR emission from lunar samples. They suggest the presence of sample proportions of Fe^{2+} which quenches luminescence. The results of the present work seem to suggest that this hypothesis cannot be correct. The

disappearance of the IR emission from shocked plagioclase samples is caused by changes of the crystal fields near the Fe^{3+} sites.

We have already noted that the emission spectrum of our "unshocked" andesine sample shows very little intensity at the wavelength of the IR emission. We suspect that this plagioclase is pure, i.e., contains very little Fe^{3+} .

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References

- Ahrens TJ, Petersen CF, Rosenberg JT (1969) Shock compression of feldspars. *J Geophys Res* 74:2727-2746
- Arndt J, Hummel W, Gonzalez-Cabeza I (1982) Diaplectic labradorite glass from the Manicouagan impact crater I: Physical properties, crystallization, structural and genetic implications. *Phys Chem Minerals* 8:230-239
- Bunch TE, Cohen AJ, Dence MR (1967) Natural terrestrial maskelynite. *Am Mineral* 52:244-253
- Bunch TE, Cohen AJ, Dence MR (1968) Shock-induced structural disorder in plagioclase and quartz. In: French BM, Short NM (eds) Shock metamorphism of natural minerals. Mono Book Corp, Baltimore, pp 509-518
- Diemann E, Arndt JL (1984) Diaplectic labradorite glass from the Manicouagan impact crater II: X-ray diffraction studies and structural model. *Phys Chem Minerals* 11:178-181
- Duke MB (1968) The Shergotty meteorite: Magmatic and shock metamorphic features. In: French BM, Short NM (eds) Shock metamorphism of natural minerals. Mono Book Corp, Baltimore, pp 613-621
- Duvall GE, Fowles GR (1963) Shock waves. In: Bradley RS (ed) High pressure physics and chemistry, vol 2. McGraw-Hill, New York, pp 209-291
- Dworak U (1969) Stosswellenmetamorphose des Anorthosits von Manicouagan Krater, Quebec, Canada. *Contrib Mineral Petrol* 24:306-347
- Engelhardt Wv, Stöffler D (1968) Stages of shock metamorphism in crystalline rocks of the Ries Basin, Germany. In: French BM, Short NM (eds) Shock metamorphism of natural materials. Mono Book Corp, Baltimore, pp 159-168
- Estep PA, Kovack JJ, Waldstein P, Karr Jr C (1972) Infrared and Raman spectroscopic studies of structural variations in minerals from Apollo 11, 12, 14, and 15 samples. *Proc 3rd Lunar Sci Conf*, MIT Press, Cambridge, pp 3047-3067
- Fabel GW, White WB, White EW, Roy R (1972) Structure of lunar glasses by Raman and soft x-ray spectrography. *Proc 3rd Lunar Sci Conf*, MIT Press, Cambridge, pp 939-951
- French BM, Short NM (eds) (1968) Shock metamorphism of natural materials. Mono Book Corp, Baltimore
- Geake JE, Walker G (1975) Luminescence of minerals in the near-infrared. In: Karr Jr C (ed) Infrared and raman spectroscopy of lunar and terrestrial minerals. Academic Press, New York, pp 73-89
- Geake JE, Walker G, Mills AA, Garlick GFJ (1971) Luminescence of Apollo lunar samples. *Proc 2nd Lunar Sci Conf*, MIT Press, Cambridge, pp 2265-2275
- Geake JE, Walker F, Telfer DJ, Mills AA, Garlick GFJ (1973) Luminescence of lunar, terrestrial, and synthesized plagioclase, caused by Mn^{2+} and Fe^{3+} . *Proc 4th Lunar Sci Conf*, pp 3181-3189
- Gibbons RV, Ahrens TJ (1977) Effects of shock pressure on calcic plagioclase. *Phys Chem Minerals* 1:95-107
- Grady DE (1980) Shock deformation of brittle solids. *J Geophys Res* 85:913-924
- Hans RE, Montague BR, Davis MK, Galindo C, Hörz F (1977) X-ray diffractometer studies of shocked materials. *Proc 9th Lunar Planet Sci Conf*, pp 2773-2787
- Hörz F (1970) A small ballistic range for impact metamorphism studies. NASA Technical Note D-5787:15
- Hörz F, Quaide WL (1973) Debye-Scherrer investigations of experimentally shocked silicates. *The Moon* 6:45-72
- Hörz F, Hans R, Serna C (1986) X-ray investigations of the shock history of the Shergottite achondrite. *Geochim Cosmochim Acta* 50:905-908
- Lal JC (1986) The Shergotty consortium and SNC meteorites: an overview. *Geochim Cosmochim Acta* 50:875-889
- Lambert P, Grieve RAF (1984) Shock experiments on maskelynite-bearing anorthosite. *Earth Planet Sci Lett* 68:159-171
- Marsh SP (ed) (1980) LASL Shock Hugoniot Data, University of California Press, p 658
- McMillan P, Piriou N, Navrotsky A (1982) A Raman spectroscopic study of glasses along the joint silica-calcium aluminate, silica-sodium aluminate and silica-potassium aluminate. *Geochim Cosmochim Acta* 46:2021-3047
- Milton DJ, DeCarli PS (1963) Maskelynite: Formation by explosive shock. *Science* 140:670-671
- Ostertag R (1983) Shock experiments on feldspar crystals. *Proc 14th Lunar Planet Sci Conf*, Supp *J Geophys Res*:B365-B367
- Sharma SK, Virgo D, Mysen B (1978) Structure of melts along the joint SiO_2 - $\text{NaAlSi}_3\text{O}_8$. *Carnegie Inst Wash Yearb* 77:652-658
- Sharma SK, Simons B, Yoder Jr HS (1983) Raman study of anorthite, calcium-Tschermak's pyroxene and gehlenite in crystalline, and glassy states. *Am Mineral* 68:1113-1125
- Sharma SK, Philpotts JA, Matson DW (1985) Ring distributions in alkali- and alkaline-earth aluminosilicate framework glasses - a Raman spectroscopic study. *J Noncryst Solids* 71:403-410
- Sippel RF, Spencer AB (1970) Luminescence petrography and properties of lunar crystalline rocks and breccias. *Proc Apollo 11 Lunar Sci Conf*, MIT Press, Cambridge, pp 2413-2426
- Smith JV (1974) Feldspar minerals. vols I and II. Springer, Berlin Heidelberg New York
- Stöffler D (1972) Deformation and transformation of rock-forming minerals by natural and experimental shock processes I: Behavior of minerals under shock compressions. *Fortschr Mineral* 49:50-113
- Stöffler D (1974) Deformation and transformation of rock-forming minerals by natural and experimental shock processes II: Physical properties of minerals. *Fortschr Mineral* 51:256-289
- Stöffler D (1984) Glasses formed by hypervelocity impact. *J Noncryst Solids* 67:465-502
- Stöffler D, Hornemann U (1972) Quartz and feldspar glasses produced by natural and experimental shock. *Meteoritics* 78:371-394
- Stöffler D, Ostertag R, Jammes C, Pfannschmidt G, Sen Gupta PR, Simon SB, Papike JJ, Beauchamp RU (1986) Shock metamorphism and petrography of the Shergotty achondrite. *Geochim Cosmochim Acta* 50:889-908
- Tschermak G (1872) Die Meteoriten von Shergotty and Gopalpur. *Sitzungsber. Akad Wiss Wien Math-Naturwiss K* 65 Part 1:122-146
- Tyburzy TA, Ahrens TJ (1986) Dynamic compression and volatile release of carbonates. *J Geophys Res* 91:4730-4744
- Velde B, Boyer H (1986) Raman microprobe spectra of shocked plagioclase feldspars. *Raman Spectrosc Earth Sci Init Appl Georaman* 86:23-24
- Virgo D, Mysen BO, Siefert F (1979) Structures of quenched melts in the system NaAl AlO_4 - $\text{CaMgSi}_2\text{O}_6$ - Mg_2SiO_4 - SiO_2 at 1 atm. *Carnegie Inst Wash Yearb* 78:502-506