Shock-compressed MgSiO$_3$ glass, enstatite, olivine, and quartz: 
Optical emission, temperatures, and melting

Sheng-Nian Luo
Plasma Physics (P-24) and Earth and Environmental Sciences (EES-11), Los Alamos National Laboratory, Los Alamos, New Mexico, USA
Lindhurst Laboratory of Experimental Geophysics, Seismological Laboratory, California Institute of Technology, Pasadena, California, USA

Joseph A. Akins and Thomas J. Ahrens
Lindhurst Laboratory of Experimental Geophysics, Seismological Laboratory, California Institute of Technology, Pasadena, California, USA

Paul D. Asimow
Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, USA

Received 20 October 2003; revised 3 March 2004; accepted 10 March 2004; published 11 May 2004.

1. Introduction

Progress in the application of modern seismic techniques ranging from travel time tomography to waveform modeling continues to yield improved knowledge of the three-dimensional structure of longitudinal and shear wave velocities and density of the Earth’s deep interior [Grand et al., 1997; Ni et al., 2002]. Converting such observations into constraints on the chemical, mineralogical, and thermal state of the mantle requires detailed understanding of the equations of state (EOS) and phase transitions (both solid-solid and melting) of candidate minerals. Of particular interest are the low- and ultra-low velocity zones (ULVZ) found in the lowermost mantle near the core-mantle boundary (CMB) [Garnero and Helmberger, 1995]. The velocity reductions associated with these anomalies are so extreme that partial melting appears to be the only interpretation allowed by mineral physics. Understanding the consequences of such melting demands detailed knowledge of phase relations and physical properties for the major (and, eventually, minor components) of the lower mantle, presumably silicates and oxides such as (Mg,Fe)$_2$SiO$_4$, (Mg,Fe)SiO$_3$, and perovskite.
(Mg,Fe)O and perhaps SiO₂. Static high-pressure experiments in the multianvil apparatus and diamond-anvil cell (DAC) have provided some constraints on the melting behavior of such minerals [Zerr and Boehler, 1993; Shen and Lazor, 1995; Heinz and Jeanloz, 1987; Kato and Kumazawa, 1985]. Limitations on the pressure and temperature capability of these systems, however, mean that melting of some of these components has not been characterized above 100 GPa; there are also major discrepancies among the measured or extrapolated melting curves derived from DAC observations for some components. First-principles and molecular dynamics simulations of such complicated silicate systems remain challenging, and at present must still be validated against accurate experimental results. In dynamic techniques such as planar shock wave loading, samples are compressed and heated simultaneously, thus melting points above 100 GPa can in principle be measured, although studies with such techniques suffer from scanty data and possible kinetic behavior such as superheating [Boness and Brown, 1993; Luo and Ahrens, 2003; Luo et al., 2003a; Luo and Ahrens, 2004]. Currently, shock wave loading serves as a major practical approach to resolving melting at pressures directly relevant to the lowermost mantle. In this work, we intend to probe the melting behavior of MgSiO₃ perovskite (hereafter, Pv) and the analogue lower mantle assemblage Pv plus periclase.

[5] No shock temperature data are available for Pv. Although we have not used Pv as an ambient pressure starting material in this study, we expect that Pv forms upon shock wave loading of MgSiO₃ glass or of crystalline enstatite at shock pressure greater than about 60 GPa [Brown et al., 1987b]. Previously, the long-range order of shocked Si and Ga has been observed [Swift et al., 2001; Luo et al., 2004] with in situ time-resolved X-ray diffraction techniques. We take this as an indication that the crystalline phases may also form during shock wave loading of silicates. As MgSiO₃ glass is less dense than enstatite at lower pressure on the principal Hugoniot of glass than on that of enstatite, and so shock-synthesized perovskite melts at lower pressure on the principal Hugoniot of glass than on that of enstatite. Both starting materials are investigated in this work in order to obtain constraints on the melting of Pv at different pressures.

[4] The shock wave equations of state [Jackson and Ahrens, 1979; Brown et al., 1987b] and high-pressure sound speed [Brown et al., 1987a] have previously been measured for forsterite and olivine. Shock melting of forsterite and olivine has been investigated using optical pyrometry to infer shock temperatures [Lyzenga and Ahrens, 1980; Holland and Ahrens, 1997]. At similar pressures, the temperatures inferred by Holland and Ahrens [1997] are significantly higher than those by Lyzenga and Ahrens [1980], possibly due to the low emissivity obtained in the former study, which also found unexplained dramatic differences in emissivities at slightly different pressures for the same phases (e.g., ε ~ 0.03 and 0.3 at 184 and 192 GPa, respectively). We have reanalyzed the olivine data of these authors accounting, for the first time, for optical linear absorption of the unshocked sample through which the shock front radiation is observed.

[5] Previous studies utilizing optical pyrometry assumed gray body radiation and used whole-spectrum fitting to obtain emissivity and temperature. However, the emissivity (and blackbody spectral radiance) can be determined separately and independently at each individual wavelength from time-resolved radiation recordings [Boslough, 1985]. This approach is less susceptible to scatter of measurements among different wavelengths and is able to deal with non-gray body spectral features. This technique is of particular advantage for unshocked materials with band-like absorption spectra such as Fe-bearing olivine and orthopyroxene that complicate the radiation history of shocked samples. Besides optical properties and temperature, the radiation history contains a record of shock front velocity and hence can be inverted for equation of state, which is usually measured with different diagnostic technology. As quartz is well-studied with various techniques including shock temperature measurement, it is included in present study as a technical reference. We begin by reviewing the methodology of optical pyrometry followed by experiments and data analysis sections. We end with a discussion of the geophysical implications of these results.

2. Methodology

[6] Optical pyrometry is the use of optical emission measurements to determine the temperature and optical properties of shock-compressed materials [Komer, 1965; Boslough and Ahrens, 1989]. We review here the justification for application of Planck’s formula, typical experimental designs and methods for data reduction. We assume that the observed optical signal is thermal radiation and that the electron temperature equilibrates to that of the lattice on the timescales of shock wave loading.

[7] Photons are bosons obeying Bose-Einstein statistics (e.g., Fowles [1989]). At equilibrium, the mean occupation number of photons at certain state centered at frequency ν is 

$$N = \frac{1}{e^{\hbar c k T} - 1}$$

i.e., Planck’s formula for blackbody radiation. The energy flux per unit frequency interval is

$$J_\nu = c \epsilon \nu / 4$$

and can be converted to its counterpart in wavelength (λ) with ν = c/λ and dν = (c/λ²)dλ. The spectral radiance L₀ = J₀/π for a blackbody

$$L_\lambda = \frac{c_1}{\lambda^5} \left( e^{c_2/\lambda T} - 1 \right)$$

where

$$c_1 = 2 \hbar c^2 \approx 1.191 \times 10^{-16} \text{ W m}^2 \text{ sr}^{-1} \text{ mK}^{-1}$$

and

$$c_2 = \hbar c k \approx 1.439 \times 10^{-2} \text{ mK}$$

L₀ is essentially the energy flux per unit wavelength interval per unit solid angle (W m⁻² sr⁻¹). As a light source is not necessarily a blackbody, the spectral radiance is written in a more general form as

$$L_\lambda = \epsilon(\lambda, T) L_\lambda$$

where ε is emissivity and assumed to depend on λ and T only.
[8] To determine the temperature of a radiating sample upon shock wave compression, we need to know \( L_\lambda \) and \( \epsilon(\lambda, T) \). In practice, a multichannel pyrometer (Figure 1) is utilized to measure \( L_\lambda \) at discrete wavelengths with narrow-band-pass optical filters (~9 nm half-height bandwidth). Calibration is required to obtain the absolute values of \( L_\lambda \) with a spectral radiance or irradiance source. The latter is achieved in this work. A quartz-halogen tungsten-filament lamp with spectral irradiance \( I_\lambda \) (Figure 2; Note that the unit \( \text{Wm}^{-2}\text{sr}^{-1}\text{nm}^{-1} \) is placed in the position of the target for calibration before mounting target for shock wave loading. The optical path is kept the same for calibration and experiment. Photodetectors with ~nanosecond response time convert photon signals into voltage signals recorded as time-resolved voltages by digital oscilloscopes.

\[
L_\lambda = \frac{V_{\text{sample}}}{V_{\text{lamp}}} \frac{I_\lambda}{S_{\text{mask}}}
\]

where a linear response of the photodetector to photon flux (before saturation) is assumed.

[9] A general target assembly during shock is composed of an air gap at the driver-sample interface, some already shocked sample and some not-yet-shocked sample (denoted with subscripts air, s, and n, respectively; Figure 1). The observed \( L_\lambda \) depends on the temperature and linear absorption coefficients \( \alpha \) of all three of these elements of the system as well as the reflectivity \( \chi \) of the interfaces. Assuming local thermodynamic equilibrium, emissivity \( \epsilon \) of a non-reflecting layer of thickness \( d \) is equal to absorbance, i.e., \( \epsilon = 1 - e^{-\alpha d} \). Thus the observed spectral radiance

\[
L_\lambda = L_{\lambda, \text{air}}(1 - R_1)(1 - R_2)(1 - R_3)\epsilon_{\text{air}} e^{-\alpha_{\text{air}} d} e^{-\alpha_{\text{air}} d}
+ L_{\lambda, s}(1 - R_2)(1 - R_3)\epsilon_{\text{air}} e^{-\alpha_{\text{air}} d}
+ L_{\lambda, n}(1 - R_3) e^{-\alpha_{\text{air}} d}
\]

consists of contributions from the air gap, shocked and unshocked sample where \( L_{\lambda, s,n} \) is the quantity of main

**Figure 1.** Schematic diagram of a six-channel optical pyrometer for shock temperature measurement. Air gap may be present at driver-sample interface. Light emitted from behind shock front passes through aperture of mask. Expendable turning mirror and optics relay light to six neutral-density and narrow-band color filters. Adjustable neutral-density filters on each channel allow the dynamic range of the system to be optimized for the expected loading. The optical path is kept the same for calibration and experiment. Photodetectors with ~nanosecond response time convert photon signals into voltage signals recorded as time-resolved voltages by digital oscilloscopes.

**Figure 2.** Spectral irradiance \( I_\lambda \) of quartz-halogen tungsten coiled filament lamps S-1045 (operated at 1000 W and 8 A) and M-416 (200 W and 6.5 A), interpolated with cubic spline from calibrations by Optronic Laboratories. Here \( I_\lambda \) is defined as the power per unit wavelength intercepted by a \( 1\text{ cm}^2 \) detector, 50 cm from center of filament. Note that to apply values of \( I_\lambda \) in equations (4) and (5), one needs to convert units to power per unit wavelength per unit solid angle. Vertical dotted lines denote the wavelengths of narrow-band filters adopted in the current pyrometer. The insert shows a typical calibration record (voltage versus time) at \( \lambda = 551.0 \text{ nm} \) for S-1045.
interest. If experiments are conducted without significant sample preheating, the 3rd term on the right-hand side of equation (6) can be neglected. Interface reflectivity \( R_i = \frac{\text{C}^{l_i} - \text{C}^{l_i}}{\text{C}^{l_i} + \text{C}^{l_i}}^2 \) where \( n_i \) (i = 1, 2 and 3, denoting air – sample, shocked – unshocked sample and sample – free surface interfaces respectively) is the relative index of refraction across the interface. As \( n_i \) is wavelength-dependent and its values are not available (at high pressures), we assume \( R \sim 0 \) as in previous studies [Lyzenga et al., 1983]. For a shock state with shock velocity \( U_s \) and particle velocity \( u_p \), \( d_i = (U_s - u_p)t \) and \( d_a = d_0 - U_s t \) where \( d_0 \) is the initial sample thickness and \( t \) the time after the shock front enters the sample.

[10] Previous studies mostly assumed gray (or black) body radiation, such that at each wavelength, independent of \( \lambda \), \( L_{ab} \) is given by equation (6). The values of \( L_{ab} \) at different wavelengths then allow temperature to be determined by fitting \( L_{ab}(\lambda) \) to equation (2). This results in independent values of \( c \) at each wavelength, independent of calibration and requiring no gray body assumption. Although the principle has been described before [Boslough, 1985], this method has not previously been applied rigorously to real data.

3. Experiments

[11] We carried out shock temperature measurements on synthetic x-cut single-crystal \( \alpha \)-quartz (Adolf Meller Co.), synthetic MgSiO3 glass and natural enstatite (Table 1 and 2). Our primary interest here is in the MgSiO3 system, but given the significant amount of shock wave data available for quartz [Lyzenga et al., 1983], we conducted a diagnostic quartz shot to test the pyrometer and the new data reduction technique and to provide a reference for data analysis in unknown experiments. MgSiO3 glass is synthesized by melting an equimolar mixture of Johnson-Matthey high-purity MgO and SiO2 powders at 1650°C and carefully regulating the water-quench procedure to suppress both cracking and forsterite crystallization. The natural enstatite samples are cut from gem quality single crystals from Sri Lanka. Electron microprobe analysis on both glass and enstatite revealed chemical compositions of essentially MgSiO3 (Table 1). Both MgSiO3 glass and enstatite are colorless and nearly transparent to visible light. We measured their absorption spectra in the range of 300–1100 nm (Figure 3). The absorbance of MgSiO3 glass decreases with \( \lambda \) but cannot be described by \( \lambda^{-3} \) as in Rayleigh scattering [Jackson, 1975]. Enstatite demonstrates three absorption peaks with a pronounced one near 900 nm as expected [Burns, 1993]. Note that the values for absorbance vary with optical setup and sample thickness, and are meaningful only in a relative sense.

[12] Samples are sectioned into disks and polished to appropriate thickness to minimize edge effects. Both sides are of submicron-micron smoothness, and one side is coated with a thin Al layer by evaporation. The coated side of the sample is then glued in tight contact with a finely polished metal driver plate. An air gap of varying thickness forms at the driver-sample interface. The Al coating is intended to block radiation from the shocked air gap into the sample, but its effectiveness strongly depends on the strength of coating. The air gap can be minimized by improving further the polish on the contacting surfaces of sample and driver plate. (As shown later, the effect of the air gap can be resolved in our experiments, possibly yielding extra information on the shock behavior of air.)

[13] The calibration lamp (S-1045 for quartz, MgSiO3 glass and enstatite shots) is placed at the sample position prior to installing target. A typical calibration voltage trace is shown in Figure 2 (insert) from which \( V_{\text{lamp}} \) is determined as offset of the plateau from the baseline. Then the target assembly is installed without altering the optical path and the chamber is closed and evacuated for shooting on the two-stage light-gas gun at Caltech. Each pyrometer channel output is recorded by 2–4 oscilloscope channels. The voltage signal \( (V_{\text{sample}}) \) is then converted to apparent spectral radiance \( L_\lambda \) using the calibration voltage \( V_{\text{lamp}} \), the lamp spectral irradiance \( I_\lambda \) (Figure 2), the mask area and equation (5). Figure 4 displays representative time-resolved spectral radiances of shocked MgSiO3 glass (shot 335) recorded by the six-channel pyrometer.

[14] As we will reanalyze the previous data on olivine [Holland and Ahrens, 1997], we briefly discuss the experi-
iment. Samples were San Carlos and Burma peridot with compositions close to (Mg 0.9Fe0.1)2SiO4. Optical spectroscopy of starting materials revealed a slight decrease of absorbance with wavelength in the 450–560 nm range, a shallow increase at 560–700 nm and a significant increase beyond 700 nm [Holland, 1997]. The experiment was similar to those for quartz, MgSiO3 glass and enstatite except that the calibration lamp was M-416 (Figure 2). Previous experiments on forsterite [Lyzenga and Ahrens, 1980] adopted similar technique.

4. Data Analysis

Typical spectral radiance histories of quartz, olivine, MgSiO3 glass and enstatite are shown in Figures 4 and 5. As we will see, some of the distinctive appearances of these spectra result from the differing absorbance properties of the unshocked sample materials; some features result from imperfect emission by the shocked sample early in the experiment when the shocked layer is very thin; other features result from differences in the intensity of the air

![Figure 4](image1.png)

**Figure 4.** Representative time-resolved radiance profiles recorded by the six-channel pyrometer (MgSiO3 glass, shot 335). Times marked a – e correspond to key events discussed in text upon loading and unloading.

![Figure 5](image2.png)

**Figure 5.** Time-resolved spectral radiance from (a) shocked quartz (shot 334), (b) olivine (245) and (c) enstatite (342). Dotted curves denote shock recordings, and solid curves are models fits using equation (6). The fitted parameters shown on each panel. L_{\lambda,b} is given in units of 10^{13} Wm^{-3}sr^{-1}; a_\lambda and a_{\lambda} are in mm^{-1}. Values in parentheses indicate uncertainties in the fitting. In (c), points a – f denote significant events in loading and unloading history (see text) and L_{\lambda,air} = \epsilon_{\lambda,b}L_{\lambda,b,air}.
gap flash due to variations in driver and sample polishing and Al coating. To illustrate the general physical process, the interpretation of the various parts of this record is shown using lettered time markers as in Figures 4 and 5c. First, the shock reaches the rear surface of the opaque driver at point a. Some records show a sharp rise in intensity ab as the shock reverberates in the air gap at the driver-sample interface. The air is compressed to peak pressure and its temperature rises in less than 10 ns to a level significantly higher than the sample. Once the shock enters the sample, the transmission of the air radiance turns around and increases again during cd. As the shock propagates through the sample, this interval reflects the increasing thickness (and thus emissivity) of the shocked sample and the decreasing thickness and hence absorption of the unshocked sample. The shock reaches the rear surface of the sample at time d; segment de shows the temperature and radiance decrease upon release. The reason for the later rise of radiance (ef) is not clear; possibly this is due to reshock on the metal mask. The exact shape certainly depends on the optical properties at shocked, unshocked and release states. The air gap is absent in quartz and olivine shots, thus the recordings are simpler. More quantitative analysis can be obtained from equation (6) using the following procedure. [16] Fitting the observed spectral radiance to equation (6) yields \( L_{ab} \), \( a_s \) and \( a_u \) (and possibly the product \( e_{ab}L_{ab,air} \) as well) at each wavelength. Emissivity for shocked and unshocked sample can thus be calculated for various thicknesses with \( \epsilon = 1 - e^{-a_l} \). To obtain temperature, we fit \( L_{ab} \) at various wavelengths to equation (2). Note that this neither assumes a gray body spectrum nor need it imply that the material is a blackbody emissivity is separated from spectral radiance and the fitting of \( L_{ab} \)'s to equation (2) represents the true temperature. [17] Besides temperature and optical properties (linear absorption coefficients), the shock wave velocity \( U_s \) can also be deduced from the spectral radiance history as \( U_s = d_0/\Delta t \) where \( \Delta t = t_2 - t_1 \) is shock travel time across a distance \( d_0 \) (Figures 5a and 5b where the air gap is absent). On records showing a flash from the air gap \( t_1 \) is obscured and times \( b \) and \( d \) are chosen as \( t_1 \) and \( t_2 \), respectively (Figure 5c). The flyer plate velocity (\( U_{fp} \)) is obtained from flash X-ray radiography. Without assuming an equation of state (e.g., \( U_s - U_{fp} \) relation) of the sample material, the pressure \( P_H \), density \( \rho \) and \( U_{fp} \) at shock state can be obtained from the impedance match method (jump conditions)

\[
\rho_0 A U_s U_{fp} = \rho_0 B [C_{oB} + s_B (U_{fp} - U_s)] (U_{fp} - U_s)
\]

\[
P_H = \rho_0 A U_s U_{fp}
\]

\[
\rho_d = \rho_0 A U_s / (U_s - U_{fp})
\]

where subscript 0 refers to initial condition, A refers to the sample and B denotes the driver (or, equivalently, the flyer as both driver and flyer are Ta plates). Parameters \( C_{oB}, s_B \) and \( \rho_0 B \) are known for Ta standard [Mitchell and Nellis, 1981]. Results are summarized in Table 2.

### 4.1. Quartz

Complete spectral radiance signals were recorded at \( \lambda = 451.5, 602.7 \text{ and } 748.3 \text{ nm (the other three channels were off scale) during this diagnostic shot (334). There is no air radiance peak on these records, so we fit the radiance history at each of the three recorded wavelengths to}

\[
L_{\lambda} = L_{\lambda,0} \left[ 1 - e^{-a_s(U_s-U_{fp})} \right] e^{-a_u(U_f-U_{fp})}
\]

with \( L_{\lambda,0}, a_s \) and \( a_u \) being unknown parameters. The fitted values of \( a_s \) and \( a_u \) indicate that shock-synthesized high-pressure phase (stishovite-like) is essentially black (e.g., at \( d > 0.2 \text{ mm} \)) and the unshocked pure quartz is totally transparent at these three wavelengths as expected (Figure 5a). Given \( L_{\lambda,0} \) at different wavelengths, we obtain \( T_H = 6680 \pm 420 \text{ K from fitting to equation (2). The clear onset and exit times of shock transit through the sample on this record yield good values for } U_s, P_H \text{ and } U_{fp} \text{ as well (Table 2). Our } (U_s, U_{fp}) \text{ values at } P_H = 106 \text{ GPa agree with R. G. McQueen's } (U_s - U_{fp}) \text{ relationship [Lyzenga et al., 1983]: } U_s/(km/s) = 1.241(0.160) + 1.850(0.045) U_{fp}.

\[ \text{[19] Lyzenga and Ahrens [1980] obtained } \epsilon \sim 1 \text{ and } 5820 \pm 150 \text{ K at } 106.5 \text{ GPa assuming gray body radiation. Their whole-spectrum fitting indicates the high-pressure phase is blackbody like, consistent with our values of } a_s \text{ from non-linear fitting to the radiation history obtained in our separate shot. If the unshocked material is totally transparent and the shock-synthesized phase black as appears to be the case for quartz, the two methods of fitting ought to yield the same result. Our current measurement of } T_H = 6680 \pm 420 \text{ K matches a shock temperature calculation (} T_H = 6650 \text{ K at } 106 \text{ GPa) [Luo et al., 2003b] that used an independent measurement of the high-pressure Grüneisen parameter of stishovite [Luo et al., 2002b]. The new}

### Table 2. Shock Wave Experiments Parameters

<table>
<thead>
<tr>
<th>Shot #</th>
<th>Starting Material</th>
<th>( d ) (mm)</th>
<th>( \phi ) (mm)</th>
<th>( \rho_0 ) (g/cm(^3))</th>
<th>( U_s ) (km/s)</th>
<th>( P_H ) (GPa)</th>
<th>( U_f ) (km/s)</th>
<th>( U_{fp} ) (km/s)</th>
<th>( \rho ) (g/cm(^3))</th>
<th>( T_H ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>245</td>
<td>Olivine</td>
<td>3.38</td>
<td>6.35</td>
<td>3.36</td>
<td>6.82</td>
<td>188(6)</td>
<td>11.46(16)</td>
<td>4.89(15)</td>
<td>5.86(15)</td>
<td>4810(70)</td>
</tr>
<tr>
<td>334</td>
<td>Quartz</td>
<td>4.78</td>
<td>2.11</td>
<td>2.65</td>
<td>5.64</td>
<td>106(1)</td>
<td>9.23(7)</td>
<td>4.36(4)</td>
<td>5.02(5)</td>
<td>6680(420)</td>
</tr>
<tr>
<td>335</td>
<td>En. Glass</td>
<td>3.85</td>
<td>2.02</td>
<td>2.75</td>
<td>5.67</td>
<td>117(3)</td>
<td>9.85(10)</td>
<td>4.30(8)</td>
<td>4.88(8)</td>
<td>5580(130)</td>
</tr>
<tr>
<td>336</td>
<td>En. Glass</td>
<td>2.54</td>
<td>2.10</td>
<td>2.73</td>
<td>5.88</td>
<td>121(4)</td>
<td>9.92(16)</td>
<td>4.47(13)</td>
<td>4.96(13)</td>
<td>5940(560)</td>
</tr>
<tr>
<td>340</td>
<td>En. Crystal</td>
<td>1.86</td>
<td>2.02</td>
<td>3.19</td>
<td>5.85</td>
<td>142(7)</td>
<td>10.47(24)</td>
<td>4.26(18)</td>
<td>5.38(17)</td>
<td>4130(50)</td>
</tr>
<tr>
<td>341</td>
<td>En. Crystal</td>
<td>1.88</td>
<td>1.98</td>
<td>3.19</td>
<td>6.38</td>
<td>165(8)</td>
<td>11.17(27)</td>
<td>4.62(20)</td>
<td>5.44(19)</td>
<td>4900(140)</td>
</tr>
<tr>
<td>342</td>
<td>En. Crystal</td>
<td>1.95</td>
<td>1.98</td>
<td>3.23</td>
<td>6.79</td>
<td>183(9)</td>
<td>11.59(28)</td>
<td>4.89(21)</td>
<td>5.59(20)</td>
<td>5450(100)</td>
</tr>
</tbody>
</table>

\(^a\)Flyer and driver are Ta plates. Values in parentheses denote uncertainties. Errors in \( d, \rho_0 \) and \( U_s \) are negligible. \( \phi \) is the diameter of the aperture in the mask.
4.2. Olivine (Mg,Fe)2SiO4

[20] Shock temperature experiments on (Mg0.9, Fe0.1)2SiO4 olivine (denoted as Fo090) [Holland and Ahrens, 1997] and Mg2SiO4 forsterite (Fo100) [Lyzenga and Ahrens, 1980] were previously conducted. However, Holland and Ahrens [1997] used the conventional gray body method of determining, which as we have emphasized is sensitive to calibration errors and can be confounded by spectral features of unshocked and shocked samples. Here we apply our calibration-independent fitting technique for a, and a0, to reanalyze data from shot 245 on olivine (Figure 5b) [Holland, 1997]; this is the only shock-temperature recording of a Fo090 experiment that yielded data of sufficient quality for the present analysis technique. Time-resolved radiance signals were obtained at five wavelengths (Figure 5b). These recordings did not give flat-topped spectral radiance signals, indicating that absorption by unshocked material is significant and that an arbitrary choice of time window for gray body fitting could yield inaccurate results. Like the quartz data presented above, the initial flash from air radiance is absent. Thus we fit the observed spectral radiance to equation (8) (Figure 5b). The fitted a0(λ) agrees with the measured absorption spectrum of the unshocked olivine [Holland, 1997]. We obtain Psh = 188 GPa and Us = 11.46 km/s (Table 2), which agree well with the known Hugoniot EOS of olivine, Us(km/s) = 6.56(0.33) + 1.01(0.08) up [Brown et al., 1987b], at the value of up = 4.89 km/s given by the impedance match.

[21] However, for shock temperature, fitting our values of Lv, to equation (2) results in TH = 4810 ± 70 K, which is significantly lower than the previous result of 6092 ± 310 K [Holland and Ahrens, 1997], but similar to the forsterite result of Lyzenga and Ahrens [1980] at slightly lower pressures. The relationship of our result to these previous gray body fitting studies can be understood by exploring the behavior of emissivity of the shocked sample (εs) and the effective emissivity (εeff) observed at the free surface (Figure 6). εs increases with thickness: εs = 1 − e−a(Us−up)ds. As shown in Figure 6a, ε ~ 1 at ds > 1 mm (i.e., at ≥150 ns shock travel time) for these five wavelengths. This indicates that the shocked olivine is essentially blackbody at ds > 1 mm which is in contrast to ε = 0.23 reported by Holland and Ahrens [1997]. Corrections are not made for other olivine shots due to the poor quality of recordings, but we expect that the reported values of TH should have been much lower.

[22] If the observed radiance resulting from emission in the shocked sample and absorption in the unshocked portion of the sample were to be interpreted as radiation from a single gray body, the result would be characterized by an effective emissivity εeff = [1 − e−a(Us−up)ds]e−a(Us−uth). For gray body fitting to the net radiation emerging from the experiment to be appropriate, it is necessary that each channel give the same value of εeff throughout the analyzed time window. As seen from Figure 6b, the effective radiance calculated with our fitted values of a, a0, and other parameters is not gray body until the very end of the record, when the shock exits at the free surface and hence absorption by the unshocked material vanishes. Thus it is not appropriate to use the last 100-ns record for gray body fitting [Holland and Ahrens, 1997] – the observed radiance in this window is band-like due to the absorption spectrum of unshocked olivine.

[23] We expect that the ε ~ 1 given by our analysis of shot 245 is in fact typical for the high-pressure assemblage of either shocked Fo90 or Fo100, despite the emissivities in the range of 0.53–0.66 obtained by Lyzenga and Ahrens [1980] using gray body fitting. The published oscilloscope traces shown by Lyzenga [1980] indicate plateau-like radiation histories in the three shots between 150–175 GPa similar to that for quartz (Figure 5a), implying that the shocked sample is blackbody like and the unshocked
4.3. MgSiO₃ Glass, Enstatite, and Air

Figure 11 below. Temperatures for shocked forsterite (see discussion and hence implies that they should have reported lower emissivity values resulting from their fitting were too low. Did report temperatures, our interpretation suggests that the range 150–175 GPa where the melting transition on the Hugoniot. For the three shots in Figure 8 shows a record for forsterite of shock-synthesized perovskite from MgSiO₃ glass and enstatite may be regarded as blackbody once the thickness of shocked material exceeds ~0.1 mm, i.e., after ~10 ns of shock transit time (Figure 7b). [25] Figure 8 displays a representative blackbody fitting of Lₙₙ₁ₚ at six wavelengths to equation (2) for shock temperature of enstatite (shot 340). For comparison we also show a conventional two-parameter gray body fit (at shock exit Lₙₙ₁ₚ ~ Lₙ, so both fits use the same data points). It is not surprising that the two-parameter gray body fit matches the data better than the one-parameter blackbody fit, but the former yields an unphysical value of ε = 1.57 ± 0.44 and a procedures that failed to eliminate the air-gap or produce a sufficiently opaque aluminized surface on the sample. Thus we fit the data to

\[ L_\lambda = L_{\lambda,\text{air}} \varepsilon_\text{air} e^{-\alpha_\lambda du} e^{-\alpha_\lambda ds} + L_{\lambda,\text{b}} (1 - e^{-\alpha_\lambda du}) e^{-\alpha_\lambda ds} \]  

where \( d_s = (U_a - u_a) t \) and \( d_u = d_0 - U_a t \). Two extra parameters \( (L_{\lambda,\text{air}} \text{ and } \varepsilon_\text{air}) \) compared to the quartz and olivine cases considered above are required to describe the radiation from the air gap. Because the shock reverberates to a peak pressure within the thin air layer, \( d_\text{air} \) cannot be determined like \( d_s \) and \( d_u \). Instead, \( L_{\lambda,\text{air}} \text{ and } \varepsilon_\text{air} \) are coupled as a single parameter \( L_{\lambda,\text{air}} \) in the fitting. The fitted values of \( a_\lambda \) reproduce the absorption spectra of the unshocked materials (for enstatite, compare Figure 3 and 7a). The large values of \( a_\lambda \) indicate that, at these six wavelengths, the shock-synthesized perovskite from MgSiO₃ glass and enstatite may be regarded as blackbody. Gray body fitting to same data should yield emissivities as blackbody. Gray body fitting to same data should yield unphysical or inaccurate emissivities due to the trade-off between the two parameters. The point here is that even in cases where the gray body assumption is valid, the numerical fitting does not necessarily yield real emissivity and temperature (see the example in the MgSiO₃ section below). Lyzenga [1980] showed a record for forsterite shocked to 140 GPa, in which continuously decaying radiation without any plateau was interpreted as being due to air gap and the low emissivity of shocked sample; no temperature was inferred from this data. While the 140 GPa shot may in fact indicate a low emissivity of Fo₁₀₀ at this condition, the result is ambiguous and further low-pressure shots are warranted to resolve this issue as well as to capture the melting transition on the Hugoniot. For the three shots in the range 150–175 GPa where Lyzenga and Ahrens [1980] did report temperatures, our interpretation suggests that the emissivity values resulting from their fitting were too low and hence implies that they should have reported lower temperatures for shocked forsterite (see discussion and Figure 11 below).

4.3. MgSiO₃ Glass, Enstatite, and Air

[24] The spectral radiance histories for shocked MgSiO₃ glass (e.g., Figure 4) and crystal enstatite (e.g., Figure 5) demonstrate air-radiance peaks, due to sample preparation sample is transparent. As the gray body assumption itself is valid (we regard blackbody as a special case of gray body), we expect the two-parameter fitting should yield emissivity close to 1, to be consistent with the radiation history. However, with a small number of channels, scatter in the data, and possible systematic errors, gray body fitting can easily yield unphysical or inaccurate emissivities due to the trade-off between the two parameters. The point here is that even in cases where the gray body assumption is valid, the numerical fitting does not necessarily yield real emissivity and temperature (see the example in the MgSiO₃ section below). Lyzenga [1980] showed a record for forsterite shocked to 140 GPa, in which continuously decaying radiation without any plateau was interpreted as being due to air gap and the low emissivity of shocked sample; no temperature was inferred from this data. While the 140 GPa shot may in fact indicate a low emissivity of Fo₁₀₀ at this condition, the result is ambiguous and further low-pressure shots are warranted to resolve this issue as well as to capture the melting transition on the Hugoniot. For the three shots in the range 150–175 GPa where Lyzenga and Ahrens [1980] did report temperatures, our interpretation suggests that the emissivity values resulting from their fitting were too low and hence implies that they should have reported lower temperatures for shocked forsterite (see discussion and Figure 11 below).
Figure 9. $U_r - U_p$ relations for shocked MgSiO$_3$ glass and enstatite from this work (squares) and Akins [2003] (circles). Solid lines are linear fits in P$_r$ regime beyond which P$_v$ melts with positive (on glass Hugoniot) and negative (on enstatite Hugoniot) Clausius-Clapeyron slopes. Note that enstatite data from radiation history (open squares) agree with Akins [2003] within experimental uncertainties. In general, the uncertainties in $U_r$ and $U_p$ from radiation history are larger than those from streak-camera diagnostics as employed in Akins [2003]. (Some error bars are smaller than the symbol size.)

lower temperature $T_H = 3820 \pm 190$ K (compared to $T_H = 4130 \pm 50$ K for the blackbody fit). This exercise demonstrates that whole-spectrum grey body fitting to data of the spectral resolution and precision available in this kind of experiment can easily yield unphysical or inaccurate results. We are concerned that this kind of trade-off may have affected reported temperature values in previous shock temperature studies (e.g., the forsterite experiments of Lyzenga and Ahrens [1980] discussed above) and we recommend the current time-resolved absorption analysis as an alternative.

[26] All three enstatite crystal experiments (340–342) yield fits with estimated uncertainties in $T_H$ that are less than 3%. The values of $T_H$ increase monotonically with shock pressure in the range 142 to 183 GPa (Figure 9). Of the two experiments on enstatite glass, shot 335 yields a result with an uncertainty of $\sim 2\%$, but the fit for glass shot 336 is based on only two channel recordings and so yields an uncertainty of $\sim 10\%$. Most likely, $T_H$ increases with $P_H$ in this case, but the difference is not significant. Note that all the uncertainties in $T_H$ reported here are only from the blackbody fitting itself – certainly other possible random or systematic error sources could be contributing as well.

[27] We also deduce values for $P_H$, $U_r$, and $U_p$ from the radiance histories (Table 2). $U_r - U_p$ pairs for MgSiO$_3$ glass and enstatite were measured from independent shock wave experiments with streak-camera diagnostics [Akins, 2003] which are shown as circles in Figure 9 along with our new results (squares). Note that there are apparent slope changes (indicated by arrows) on both glass and enstatite Hugoniots near $u_p = 4.23$ and 4.72 km/s, respectively. As the density on Hugoniot $\rho_H = \rho_0/(1 - u_p/U_r)$, such slope changes in $U_r - U_p$ indicate phase changes with density increase on glass Hugoniot and decrease on enstatite Hugoniot [McQueen et al., 1970]. In P$_r$ regime, $U_r(km/s) = 4.29(0.27) + 1.22(0.08)$ $u_p$, (glass, $\rho_0 = 2.73$ g/cm$^2$; $u_p < 4.23$ km/s) and $U_r(km/s) = 4.63(0.12) + 1.43(0.04)u_p$ (enstatite, $\rho_0 = 3.23$ g/cm$^2$; $u_p < 4.72$ km/s). Beyond P$_r$ regime, we interpret the phase changes as melting with positive Clausius-Clapeyron slope on MgSiO$_3$ glass Hugoniot and with negative slope on enstatite Hugoniot (also see next section and J. A. Akins et al., Shock induced melting of MgSiO$_3$ perovskite and implications for melts in Earth’s lowermost mantle, submitted to Science, 2003, hereinafter referred to as Akins et al., submitted manuscript, 2003). Recent studies (M. Murakami et al., Post-perovskite phase transition in MgSiO$_3$, manuscript submitted to Science, 2004, and T. Tsujiyama et al., Phase transition in MgSiO$_3$ perovskite in the Earth’s lower mantle, manuscript submitted to Science, 2004) have documented a solid-solid phase transition in this system, but this does not explain the density decrease on the glass Hugoniot, and the density increase based on the reported equation of state of the post-perovskite phase is inadequate to explain the density increase seen on the enstatite Hugoniot as well.

[28] Our analysis allows the effect of the air gap to be decoupled from the observed spectral radiance. The shock behavior of air is interesting by itself [Zel’ dovich and Raizer, 2002], with possible ionization, plasma, and chemical reaction effects, but this technique is unlikely to yield useful by-product information on air properties. First, the air radiance depends on driver-sample interface properties (e.g., thickness and coating) that are not necessarily reproducible. Second, the initial pressure in the air gap is unknown, since the sample chamber is pumped to vacuum but the glue holding the sample to the driver may form a partial seal. Third, the shocked thin Al coating could also contribute to the air-radiance. The spectra in the range of 450–900 nm appear band-like rather than gray, yet in the analysis the values of $L_b$ and $c_{air}$ are coupled as $L_b$ and $c_{air}$. Nevertheless, as an example, a simple blackbody fitting for shot 340 yields air temperature $T \sim 6270$ K (peak pressure $\sim 142$ GPa).

[29] Note that the emissivities of the shocked silicates are all close to 1 for the wavelengths adopted. This could be due to the combined effects of both temperature and optical roughness (grain size) of the shocked samples [Siegel and Howell, 2002]. Possibly, the latter effect is dominant.

5. Geophysical Implications

[30] Our method of obtaining linear absorption coefficients, Hugoniot temperatures, and Hugoniot equation of state data from optical radiance data provides substantial improvement in the precision and accuracy of information on the shock properties of quartz, olivine and forsterite, and its application to the MgSiO$_3$ glass and enstatite study yields new results of geophysical significance. One of the major applications of shock temperature data is the determination of melting behavior at lower-mantle conditions ($25 < P < 136$ GPa), where static high pressure data on melting are often absent or inconsistent. Here we discuss the implications of our new data and reanalysis of existing data
for possible melting scenarios of Mg-perovskite and its assemblage with MgO at lower mantle conditions based on shock wave and DAC measurements.

5.1. Underlying Logic

The inference of melting curves from Hugoniot temperature information is challenging. It is best to study materials (such as MgSiO3) that melt congruently along a single curve. We do not take into account possible variations in pressure and temperature at melting due to differences between olivine composition and the eutectic point in the high-pressure MgO-MgSiO3 binary. We also neglect the effect of solid solution in the melting F090. In the ideal case, equilibrium melting would occur and a sequence of Hugoniot temperature data would be available that capture three regimes: (1) the lower-pressure experiments should be consistent with a calculated Hugoniot for the expected solid assemblage; (2) the intermediate pressure data would achieve equilibrium partial melting states and should follow a plausible equilibrium melting curve with a lower slope \(dT_P/dP_H\) due to deposition of some of the increase in internal energy \(E_P\) into latent heat of melting, and (3) higher pressure data would again show a steep liquid-phase Hugoniot in \(P - T\) space, offset from the extension of the solid Hugoniot by a temperature drop consistent with the entropy of fusion and heat capacity of the material. In a less ideal, but common case, superheating of solids followed by disequilibrium melting occurs such that only two regimes are observed in a sequence of Hugoniot temperatures, separated by a sharp drop in temperature from the highest superheated solid state to a completely molten liquid state Hugoniot point that is on or above the melting curve [Boness and Brown, 1993; Luo and Ahrens, 2004]. Given the sparse temperature data now available for MgSiO3 and olivine compositions, neither scenario can be resolved with confidence, so the following discussion needs to entertain at least two plausible interpretations of each system.

A well-constrained solid phase Hugoniot will be great help in recognizing melting from Hugoniot temperature data. Here we briefly discuss the calculation of \(T_H\) along Hugoniots where solid-solid phase change occurs at high pressures, as is the case here for shock loading low-pressure phases (LPP) such as MgSiO3 glass, enstatite, forsterite and olivine. Suppose that the \(U_s - U_p\) relation is known in the high-pressure phase (HPP) regime. An isentropic of HPP centered at standard temperature \(T_0\) and pressure \(P_0\) (STP, denoted as subscript 0) can be constructed (e.g., with third order Birch-Murnaghan EOS given ambient bulk modulus \(K_{0b}\) and its pressure derivative \(K_{0b}'\)). Temperature along the isentrope is \(T_s = T_0 \exp(-\int_{V_0}^{V} / g dV)\) where \(V\) is volume and \(g\) is Gr"uneisen parameter. The internal energy increase along an isentrope \(\Delta e_s\) can be calculated by integrating \(P(V)\). At the same volume, the internal energy increase on Hugoniot is \(\Delta e_H = 1/2(P_H + P_0)\big(V_0 - V)\). The pressure difference between the isentrope and Hugoniot at the same volume is due to thermal pressure, assuming a Mie-Gr"uneisen-type equation of state. Thus \(T_H\) can be obtained by solving

\[
\Delta e_H = \Delta e_s + E_u + \int_{T_0}^{T_s} \gamma \, dT
\]

where \(E_u\) is the transformation energy from LPP to HPP at STP and can be estimated from enthalpy of formation. The constant volume heat capacity \(C_v\) can be obtained from Debye's model. For simplicity, the Dulong-Petit limit for \(C_v\) is adopted. We assume \(\gamma = \gamma_0(V/V_0)^g\). For the case Mg-SiO4 \(\rightarrow\) MgO + MgSiO3, either an isentrope for the mixture is constructed [Brown et al., 1987] or two separate isentropes are constructed with the assemblage temperature being the sum of \(T\) weighted by the mass

---

**Table 3. Parameters for Shock Temperature Calculation**

<table>
<thead>
<tr>
<th>Material</th>
<th>(K_{0b}), GPa</th>
<th>(K_{0b}')</th>
<th>(\gamma_0)</th>
<th>(H_{0b}/g)</th>
<th>(U_s - U_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO (Pe)</td>
<td>160.3</td>
<td>4.13</td>
<td>1.52</td>
<td>1.0</td>
<td>-14924</td>
</tr>
<tr>
<td>MgSiO3 (Pe)</td>
<td>260.0</td>
<td>3.7</td>
<td>1.5</td>
<td>1.0</td>
<td>-14439</td>
</tr>
<tr>
<td>Pe + Pv</td>
<td>200.0</td>
<td>4</td>
<td>1.5</td>
<td>1.0</td>
<td>-14578</td>
</tr>
<tr>
<td>MgSiO3 (Gi)</td>
<td>-14972</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgSiO3 (En)</td>
<td>-15395</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgSiO3 (Fo)</td>
<td>-15426</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(K_{0b}\) and \(K_{0b}'\) [Fei et al., 1990]; \(\gamma_0\) and \(g\) [Akins, 2003]; \(H_{0b}\) [Robie et al., 1979].

\(K_{0b}\) and \(K_{0b}'\) [Fiquet et al., 2000]; \(\gamma_0\) and \(g\) [Akins, 2003]; \(H_{0b}\) [Saxena et al., 1993].

\(K_{0b}\) and \(K_{0b}'\) [Brown et al., 1987]; \(\gamma_0\) and \(g\) (assumed); \(H_{0b}\); weighted by \(\gamma_0 = 4.10\) g cm\(^{-3}\).

\(U_s - U_p\) [Akins, 2003]; \(H_{0b}\) calculated after Richter and Bottinga [1986] and Richter [1987].

\(U_s - U_p\) [Akins, 2003]; \(H_{0b}\) [Berman, 1988].

\(U_s - U_p\) [Brown et al., 1987a]; \(H_{0b}\) [Robie et al., 1979].
state already well above the melting curve if a densely sampled data set is not available.

5.2. MgSiO$_3$ Perovskite System

[34] Existing estimates of the high-pressure melting of Mg-perovskite from DAC studies differ. Zerr and Boehler [1993] presented a fairly steep melting curve leading to an estimated $T_m$ near the CMB of ~7000 K. On the other hand, the results by Heinz and Jeanloz (1998), Knittle and Jeanloz [1989] and Sweeney and Heinz [1993] yield lower values of $T_m$, perhaps 2000–3500 K (Figure 10). Revisited data by Sweeney and Heinz [1998] agree with Zerr and Boehler [1993] at the lower pressures. Below we attempt to place additional constraints on melting of Pv using shock data.

[35] As discussed above, in both the pair of MgSiO$_3$ glass experiments and the set of three enstatite crystal experiments, we see monotonically increasing $T_H$ with $P_H$ in each set, and no break in slope among the three crystal experiments. Hence we do not directly observe melting on either $P$–$T$ Hugoniot of MgSiO$_3$. Instead, we proceed to gain some inferences from comparison of the measured $T_H$ values to calculated solid perovskite phase Hugoniots (Figure 10). The results are that, if the Hugoniot pressures of the experiments are all correct, then the MgSiO$_3$ glass points (including the well-constrained experiment at point b) are $\Delta T \sim 1000$ K below the perovskite Hugoniot centered on glass, whereas the enstatite crystal data are at $\Delta T \sim 500–1000$ K relative to the perovskite Hugoniot centered on enstatite (the upper one in Figure 10, which assumes $C_v = 3\lambda$). The magnitude of temperature drop that we expect for complete melting of shocked enstatite is $\Delta T^* \geq 1000$ K.

[36] The first interpretation we consider is that all the data are in the solid regime. This would provide no upper bound on the melting curve, and only a very weak lower bound from the maximum plausible amount of superheating [Luo and Ahrens, 2003, 2004; Luo et al., 2003a]. The Zerr and Boehler [1993] curve is consistent with this, but extrapolations of melting curves (e.g., HJ in Figure 10) indicate melting temperatures below 3000 K at 120 GPa are difficult to satisfy as these require $>80\%$ superheating. On the other hand, this interpretation would require either systematic overestimation of our experimental pressures or significant revisions in the parameters used to predict the solid-state HPP Hugoniots, so as to bring the data and the calculation into agreement if the data do indeed represent solid perovskite Hugoniots states. It is also inconsistent with the existence of phase transition (melting) at pressures near b and f (Figure 10) as indicated by $U_X - n_p$ relations (Figure 9).

[37] The second interpretation is that the well-constrained point b on the glass Hugoniot is partially molten and sits on the melting curve, in which case a simple extrapolation of tb would yield melting curve Pv-1 which indicates that states $d - f$ are solid. The interpretation that state b is partially molten (melt fraction $\sim 0.5–0.8$) is consistent with $\Delta T^* \sim 1000$ K for point b, since a melting point of 5580 K at this pressure would imply $\Delta T^* \sim 1300–1800$ K. This interpretation is consistent with the HPP solid perovskite Hugoniot calculated for glass, but as above would require a revision in the parameters to obtain agreement between the inferred solid states $d - f$ and the HPP Hugoniot centered on enstatite. Improved consistency would result if both solid
Hugonions were revised downwards by ~500 K. Since the same parameters go into these two calculations (except for $H_0$ for glass and enstatite, which are well-constrained), both curves would need to be revised. Among all the possibilities of varying the parameters for calculating Hugonion, the calculated $T_H$ with a revised $C_p$ of ~3.3 R [Lyzenga et al., 1983] would agree with the measurements at $d - f$ and thus support this interpretation. Again, such an interpretation is not consistent with $U_s - u_p$ observations as argued above.

The third interpretation is that $b$ is a fully liquid state above the melting curve. In this case a plausible melting curve $Pv-2$ could be constructed by assuming $\Delta T \sim \Delta T'$ for experiment $h$, in which case $T_m = \Delta TC_p/\Delta S_p$ and $C_p/\Delta S_p \sim 3/n2 \text{ imply } T_m \sim 4300 \text{ K (state c).}$ The resulting melting curve through $t - c$ passes close to the enstatite crystal Hugoniot point $f$, which could then plausibly be either superheated or partially molten. In this case $d$ is most likely in solid state and $e$ close to the melting curve, i.e., partially molten or solid. The disagreement between solid Hugoniot data and the calculated solid HPP Hugoniot in this case would also be ~500 K. $Pv-2$ seems plausible as the interpretation of shock temperature is consistent with melting near $b$ and $f$ as suggested by $U_s - u_p$, but its Clausius-Clapeyron slope near $f$ is positive instead of negative as suggested by $U_s - u_p$ relation.

The $U_s - u_p$ relations (Figure 9) suggest that melting with density decrease and increase occurs at pressures near $b$ and $f$, respectively. Thus a consistent interpretation of shock temperatures and $U_s - u_p$ relations is that the melting curve passes near $b$ with positive Clausius-Clapeyron slope and $f$ with negative slope ($Pv-3$). Among these three candidate high-pressure melting curves of $Pv$, $Pv-1$, 2 and $Pv-3$ is constrained by both $U_s - u_p$ and temperature data, thus the most plausible; we propose that perovskite melts along $Pv-3$ with $T_m \sim 6000 \text{ K and slight density increase}$ [Akins, 2003] at the CMB.

5.3. Olivine and Forsterite Systems

$\text{Mg}_2\text{SiO}_4$ is expected to disproportionate into $\text{MgO}$ (Pe) and $\text{MgSiO}_3$ (Pv) at lower mantle conditions [Presnall, 1995]. The melting of the Pe-Pv assemblage may be directly relevant, for example to the interpretation of seismic ultralow velocity zones above the core-mantle boundary resolved from travel time and waveform observations [Garnero and Helmberger, 1995; Luo et al., 2001, 2002a]. Hugoniot state ($U_s - u_p$) and sound speed measurements on $\text{Fo}_{100}$ and $\text{Fo}_{90}$ suggest that shock-induced melting occurs at about 145–150 GPa [Brown et al., 1987a, 1987b], which indicates that shock temperature measurements in a pressure range readily achievable with a two-stage light gas gun can be used to explore melting of this assemblage. Eutectic melting of the Pe-Pv assemblage [Zerr et al., 1997] and the solidus of pyrohitite [Zerr et al., 1998] have been investigated up to 60 GPa. Shock wave pyrometry has been applied to probe the melting of forsterite [Lyzenga and Ahrens, 1980] and of olivine ($\text{Fo}_{90}$) [Holland and Ahrens, 1997] at higher pressures, but our study of emissivity and absorption suggests a need to revise the results of these studies. The voltage recordings from the latter study allow us to better define one Hugoniot temperature at ~188 GPa (Figure 11).

Our data analysis has shown that the high-pressure assemblage Pe-Pv of shocked $\text{Fo}_{100}$ is essentially blackbody like, whereas Lyzenga and Ahrens [1980] obtained gray body fits for $\text{Fo}_{100}$ with emissivity in the range of 0.53–0.66. In the following discussion, we still consider the original temperatures of Lyzenga and Ahrens [1980] for $\text{Fo}_{100}$ as well as corrected values based on $\epsilon = 1$ (Figure 11).

Compared to both methods of calculating the HPP solid Hugoniot, all the revised $T_H$ measurements are appreciably lower than reported earlier, which is consistent with the interpretation of sound speed results (as well as $U_s - u_p$) showing that all these points should be molten (Figure 11). We consider two scenarios of melting: equilibrium and non-equilibrium (with superheating). If we adopt the original temperatures of Lyzenga and Ahrens [1980], points $c - e$, then melting curve $PP-1$ is consistent with states $c$ and $d$ representing partial melting and $e$ indicating complete melting. Thus $acd$ is the segment of the Hugoniot representing equilibrium melting of the Pe-Pv assemblage. But if the solidus depression due to fayalite component is small, then state $f$ for $\text{Fo}_{90}$ seems inconsistent with such an interpretation. States $e$ and $f$ cannot both represent fully molten states (even if the melting curve has a negative slope in this region like $Pv$) as in this case the temperature drop from $e$ to $f$ cannot represent consumption of latent heat. On the other hand, if the corrected temperatures for $\text{Fo}_{100}$ (diamonds) are adopted, we can construct a superheating-melting curve $abc'f'$, i.e., with increasing Hugoniot pressure, the Pe-Pv assemblage is superheated to ~150 GPa, then melts and achieves temperature close to the melting curve ($c'$), followed by liquid Hugoniot $cf$. We thus approximate the melting curve as PP-2. The melting temperature of the Pe-Pv assemblage at olivine bulk composition at the pressure of the CMB in these two scenarios is estimated as ~4000 K and 4400 K, respectively. PP-2 is favored because it applies a consistent methodology to emissivity determination in all the data and better explains the radiation history of the Lyzenga and Ahrens [1980] experiments.

More shock wave data would help with resolving the ambiguities in these interpretations, which remain to be investigated in the future. On the basis of the arguments above, we propose that the melting temperatures at the CMB are about 6000 ± 500 K for Mg-perovskite, and 4000 ± 300 K for olivine composition undergoing eutectic melting as a Pe-Pv assemblage (Uncertainties are estimated). These values are consistent with the prediction by Boehler [2000] that liquids in equilibrium with lower mantle minerals are very rich in MgO at CMB pressures. Once experiments firmly establish these melting points, interpretation of possible partial melting zones in ULVZs at the base of the mantle will depend on constraining the lower mantle adiabat, the temperature contrast across the core-mantle thermal boundary layer, the melting temperature of core alloys, and the role of chemical heterogeneities and minor components in the D'' layer. Of particular interest is that if the lower mantle adiabat allows melting, Pv melt may be denser than its solid counterpart. This suggests that locally formed dense Pv melt (e.g., at ULVZ’s) is more resistant to upwelling
6. Conclusion

[45] Shock wave optical pyrometry experiments on MgSiO₃ glass, enstatite, olivine and quartz yield time-and-wavelength-resolved spectral radiances. The shock travel time inferred from digital oscilloscope recordings of optical radiation is consistent with previous Hugoniot equations of state measured with streak camera or other diagnostics. At each wavelength, the optical absorption coefficients and blackbody spectral radiances of the shocked and unshocked samples were obtained by fitting to the radiation history. The linear absorption coefficients indicate blackbody radiation of shock-synthesized high-pressure phases (once thickness of the shocked layer exceeds 1 mm) in the wavelength range investigated. However, unshocked crystalline enstatite and Fe-bearing olivine are shown to have absorption bands in their spectra that complicate effective gray body fitting of radiation emerging from partly shielded shock fronts. We suggest downwards revisions in the shock temperatures for olivine previously published by Lyzenga and Ahrens [1980] and Holland and Ahrens [1997]. Temperatures of shock-synthesized Mg-perovskite and its assemblage with periclase provide constraints on their high-pressure melting curves. It is suggested that Mg-perovskite melts with density increase at the CMB pressure, and that the melting temperatures at the CMB are about 6000 ± 500 K for Mg-perovskite, and 4000 ± 300 K for the Mg-perovskite-periclase assemblage.

[46] Acknowledgments. This work was supported by U.S. National Science Foundation Grant No. EAR-0207934 (TJA and PDA). SNL is sponsored by a Director’s Post-doctoral Fellowship at Los Alamos National Laboratory (P-24 and EES-11). P. Gelle, M. Long and C. McCaughhey supplied invaluable technical support. G. R. Rossman and E. Arrrondou kindly helped with optical spectroscopy measurements. C. Francis and S. Mackwell supplied the high-quality Sri Lanka enstatite crystals. We also benefited from discussions with X. L. Huang, S. D. Ni and D. C. Swift. The constructive suggestions by D. Heinz and I. Jackson are highly appreciated. Contribution No. 8951, Division of Geological and Planetary Sciences, California Institute of Technology.

References


Fei, Y., S. K. Saxena, and A. Navrotsky (1990), Internally consistent thermodynamic data and equilibrium phase relations for compounds in the system MgO-SiO₂ at high pressure and high temperature, J. Geophys. Res., 95, 6915–6928.


Jackson, J. D. (1975), Classical Electrodynamics, John Wiley, Hoboken, N. J.


