Densities of Liquid Silicates at High Pressures

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Abstract. Densities of molten silicate liquids at high pressures (up to 220 kilobars) have been measured for the first time with shock-wave techniques. For a model basaltic composition (68 mole percent anorthite and 32 mole percent diopside), a bulk modulus \( K_0 \) of ~220 kilobars and a pressure derivative \( dK_0/dP \) of ~4 were derived. Some implications of these results are as follows: (1) basic to ultrabasic melts become denser than olivine- and pyroxene-rich hosts, mantle at pressures of 6 to 100 kilobars; (2) there is a maximum depth within which basaltic melt can rise within terrestrial planetary interiors; (3) the slope of silicate liquid \( \delta K_0/\delta P \), where \( K_0 \) is the bulk modulus, may become as steep as high pressures; and (4) enriched mantle reservoirs may have developed by downward segregation of melt early in Earth history.

Knowledge of the properties of silicate liquids at high pressures and temperatures is fundamental to our understanding of the differentiation processes that occur within planetary interiors. Using the falling-sphere technique, Fujii and Kushiro determined the densities of a variety of silicate liquids up to 30 kilobars into piston cylinder apparatus. Liquid silicate densities at high pressures have also been calculated by estimation of their elastic properties. We report here the first shock-wave measurements of the densities of silicate liquids at high temperatures and pressures, extending by more than an order of magnitude (to 235 kilobars) the maximum pressure at which the densities have been determined. Our motivations for this work included the following:

1) The rates of melt migration and segregation within partially molten epochs in planetary interiors depend on the difference in density between the melt and the coexisting solids. In addition, the sign of the density contrast between the melt and the coexisting residual crystals determines whether the melt will migrate upward or downward. (2) Magma may move away from the source by percolation, in cracks, or as diapirs. In each of these cases, the density contrast between melt and solid enters into the velocity with which the magma moves and thus places important constraints on the thermal and chemical evolution of rising (or sinking) magmas.

2) The slope of the solids, \( \delta K_0/\delta P \), where \( K_0 \) is the bulk modulus and \( P \) is pressure, depends upon \( \delta V \), the volume change of the reaction defining the solids. Thus the pressure dependence of the density contrast between coexisting phases along the solids is an important factor in the variations of the position of the solids with pressure and consequently in the melting behavior of planetary mantles.

3) The structures of silicate melts at high pressures and temperatures have been predicted by molecular dynamics simulations. These simulations also model the density and transport properties of silicate melts (D). Density measurements at high pressures can be compared with those derived from the simulations to place constraints on the interatomic potentials that are critical to the calculations and hence to refine calculated structural models and transport properties.

The composition that we used for our initial experiments is the anorthite-diopside (85 mole percent anorthite and 15 mole percent diopside) bulk modulus \( K_0 \) of ~220 kilobars and a pressure derivative \( dK_0/dP \) of ~4 were derived. Some implications of these results are as follows: (1) basic to ultrabasic melts become denser than olivine- and pyroxene-rich hosts, mantle at pressures of 6 to 100 kilobars; (2) there is a maximum depth within which basaltic melt can rise within terrestrial planetary interiors; (3) the slopes of silicate liquid \( \delta K_0/\delta P \), where \( K_0 \) is the bulk modulus, may become as steep as high pressures; and (4) enriched mantle reservoirs may have developed by downward segregation of melt early in Earth history.

The pressure and density (\( d \)) of a material at shock-wave experiments are determined from the Rankine-Hugoniot equations (6). The shock wave is generated by a 1.2-mm-diameter steel flyer plate that has been accelerated to high velocity (1 to 2.5,000 m/sec) in a 40-cm propellant gun (7). A schematic representation of the experimental target, just prior to projectile impact, is shown in Fig. 1 (6, 9). During these experiments, the quantities measured are shock velocity \( U \) and particle velocity \( u \). One can calculate the 1-atom density \( n \) (by using partial molar volumes reported by Nelson and Carmichael (10). The particle velocity is determined by measurement of projectile velocity and subsequent impedance mismatch with the sample (9). One obtains the shock velocity by measuring the time difference between the entrance end exit of the shock front through the sample (11, 12).

The results shown in Table 1 illustrate that a material can be fit by a straight line given by

\[ U = 2.94 + 0.05 \text{ km/sec} \times d \]

(1.29 ± 0.08s).

This experimental fit to the Hugoniot is shown in the inset of Fig. 2. From the analysis developed by Rudolf (13), we calculate an insonic, 1-atom bulk modulus, \( K_0 \) or \( \alpha P_0 \), 226 ± 8 kilobars, and a pressure derivative, \( \delta K_0/\delta P \), 4.15 ± 0.24. The value of \( K_0 \) is in good agreement with the values calculated from the measured ultrasonic velocity (221 to 231 kilobars (5, 14)). For typical mantle minerals, \( K_0 \) is 1.2 to 2.1 mbar and \( \delta K_0/\delta P \) ~4.7.

With increasing pressure, crystalline silicates undergo phase changes leading to abrupt increases in the structure transforms for iron and nickel at elevated P. Waff (16) suggested that similar abrupt increases in \( P \) would occur in silicate liquids as coordination changes such as \( \langle Al^3+ \rangle \rightarrow \langle Al^2+ \rangle \) and \( \langle Si^4+ \rangle \rightarrow \langle Si^3+ \rangle \) occurred. However, silicate liquids could achieve substantial cosp ace.
Table 1. Molen Ano Hugoniot data (T0 = 100°C, P0 = 3.05x10^5 cmHg).

<table>
<thead>
<tr>
<th>Shot No.</th>
<th>River pine material</th>
<th>Impact velocity (m/sec)</th>
<th>Shock velocity (km/sec)</th>
<th>Particle velocity (km/sec)</th>
<th>Hugoniot pressure (kbar)</th>
<th>Hugoniot density (g/cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>592</td>
<td>Al</td>
<td>1.05 ± 0.02</td>
<td>5.59 ± 0.04</td>
<td>0.44 ± 0.01</td>
<td>41.0 ± 0.5</td>
<td>2.07 ± 0.02</td>
</tr>
<tr>
<td>593</td>
<td>Al</td>
<td>1.50 ± 0.03</td>
<td>6.65 ± 0.04</td>
<td>0.65 ± 0.02</td>
<td>65.0 ± 1.4</td>
<td>3.17 ± 0.03</td>
</tr>
<tr>
<td>65</td>
<td>Wal</td>
<td>7.00 ± 0.06</td>
<td>4.36 ± 0.10</td>
<td>0.88 ± 0.02</td>
<td>93.0 ± 2.9</td>
<td>3.31 ± 0.04</td>
</tr>
<tr>
<td>467</td>
<td>W</td>
<td>1.80 ± 0.01</td>
<td>7.20 ± 0.05</td>
<td>1.73 ± 0.07</td>
<td>2.68 ± 5.0</td>
<td>3.95 ± 0.05</td>
</tr>
</tbody>
</table>

by a continual diminution of the trihydrous network or by gradual condensation changes rather than by the abrupt condensation changes characteristic of solids. Rampe spectroscopy carried out on glasses quenched from SIotic melts at P up to 80 kbar does indeed suggest that the AlO6-O-AlSi bond angles in the trihydrous network decrease contin- uously and that at this P aluminum and silicon are still essentially entirely in trihydrous coordination (7). Recent nuclear magnetic resonance results from albite glasses quenched from melts at high pressures suggest that, when AlII enters sixfold coordination in melts, it does so over a wide P range (18). Molec- ular dynamics simulations have also sug- gested that structural changes in melts and especially Al2O3 and aluminum oxo- coordination numbers, change gradually and continuously as pressure increases to several hundred kilobars (9) rather than already over narrow P intervals (19). Our results are consistent with gradual and continuous structural changes, since the data can be fit by a single compression curve in straight line in lP (q-space). In addition, the unexpect- edly low value of ki in L (l) can be rational- ized on the basis of continuous structural changes taking place in the melt with increasing P. These results have some far-reaching implications for differentiation within terrestrial planetary interiors by igneous processes. 11. Using the values of k1 and k2 derived from our experiments (20), we pre- dict that the density of velocity fields, basic to ultramafic melts of the mantle, would override the bulk density of the
residual solid at moderate P to 100 kbar. Basaltic liquid composition curves fall within the hatched band in Fig. 2. The range of kPa of p values corresponds to that expected for picritic end-members (ridge basalt (2.7 g/cm³) to komatiite (2.3 g/cm³) at their solidi (21-23). The liquids become denser than magmas of olivine and orthopyroxene, which are probable residual phases, at P from 40 to 60 kbar. Furthermore, the liquids become denser than the bulk mantle [derived from whole Earth seismological models (24, 25)] between 60 and 100 kbar. We propose that the lack of density contrast between melt and coexisting solid over this P range could lead to stabilization of partially molten zones in the upper part of the low-density zone of the present Earth (2).

2) There is a maximum depth from which volatile-poor basaltic magma produced by partial melting of ultrabasic mantle material can be derived, the estimate of this depth is based on the requirement of a positive density contrast to drive upward melt migration (2). For Earth and Venus, assuming an average I-una basaltic magma density of 2.75 g/cm³ derived from a mantle where Mg/(Fe + Mg) = 0.9 (26), this depth is about 300 km. For Mars, a much smaller planet, which may have a more iron-rich mantle (Mg/(Fe + Mg) = 0.7 to 0.4), this depth would be much greater, about 1000 km. Internal pressures within the moon are not expected to be high enough to lead to a dense crossover for a primitive basaltic composition (29).

3) A decrease in the density contrast between liquid and solid cooling solids is expected to lead to a decrease in the slope of the solids (dT/dP), which, in the absence of excess volatiles, is positive for an olivine-bearing rock as a function of pressure (29). For constraint melting of a single mineral, the slope of the solidus flattens with increasing P as dV/dr = 0. For incongruent melting, melting involving solid solutions, or melting of a polymorphic assemblage, however, dT/dP may be positive even though the melt density is less than or equal to all of the residual solid phases. Thus, care must be taken in using our results to infer the slope of a peridotite solidus at high P, since a very dense phase, garnet, is an important participant in likely melting reactions and since the liquid composition at peridotite solidus is not well known at high P. If the slopes of the source rock and basalt solidus remain positive and are greater than the prevailing geothermal gradient, any decrease in the density contrast between liquid and solid will begin to crystallize and presumably not move very far. However, if the slopes of the solidus do become flat or negative, there could be an increase in the amount of melt with increasing depth, both from concentration of downwelling-potential liquids and from the decrease in solidus temperatures.

Our analysis implies that the slopes of the solidus of conservatively melting silicates with ortho-pyroxene (Sp) (for example, MgSi₂O₆ perovskite) at high pressures are less than those of silicates found in the slatite mantle (dT/dP) at constant volume at 1170°C for silicate I (29) and that their solidi may indeed become less steep. Recent shock temperature measurements confirm this; for spinolite at 700 kbar and 420°C, dT/dP was inferred to be 1.1 ± 0.5 kbar (30). Extrapolating our results, we calculate that the density of liquid MgSi₂O₆ at 3000°C would increase from 2.37 to 4.00 g/cm³ at 400 kbar (31). At 1000 kbar, MgSi₂O₆ perovskite would have a p of 4.63 g/cm³ at room temperature and 4.10 g/cm³ at 3000°C (2). If we assume congruent melting and an entropy of melting of ~8.6 J/mole-atom K (25, dT/dP = 0.1°C per kbar. With the melting-point estimate of Obs- Sp (34) for MgSi₂O₆ perovskite at 290°C, we can estimate the melting point at 400 kbar to be ~350°C. Despite the substantial extrapolations required for this calculation, we suggest that there may be a maximum in the solidus of perovskite in the vicinity of 400 kbar and that, at the very least, the slope of the solidus will be very small. This further supports the view that the temperature of the lower mantle is constrained to be <500°C in the absence of partial melt.

4) A melt phase may become more dense than its surroundings at high P but not only for the possibility of resultant magma within planetary interi- ors but also for concentrating it at depth by downward segregation. Some implications of a laterally extensive, dense, magmatic melt layer for the genesis of komatiites were recently discussed by Nebe and Walker (22). Stolper and his co-workers (2) and Oberti (4) also discussed possible implications of dense melt at depth for mantle lithospheric garnets. During early Earth history when the heat production from radioactive decay was presumably higher than today (35), it is likely that there was a higher degree of partial melting globally and that it extended to greater depths than in the present Earth. Because the likely dominant residual minerals, olivine and ortho- pyroxene, were expected to form basic melts at pressures greater than ~40 to 70 kbar, stable chemical fractionat-