Shock compression of preheated silicate liquids: Apparent universality of increasing Grüneisen parameter upon compression

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SHOCK COMPRESSION OF PREHEATED SILICATE LIQUIDS: APPARENT UNIVERSALITY OF INCREASING GRÜNEISEN PARAMETER UPON COMPRESSION

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Abstract. Shock compression experiments achieving \( \geq 100 \) GPa pressures are available for seven silicate liquid compositions in the system CaO-MgO-FeO-Al\(_2\)O\(_3\)-SiO\(_2\). Especially when liquid states have been sampled along multiple Hugoniots, these data are sufficient to evaluate the dependence of Grüneisen \( \gamma \) on volume in silicate liquids. The increase in \( \gamma \) upon compression in these liquids is a surprising feature, but this behavior is seen consistently in all studied compositions, by multiple experimental techniques and also in \textit{ab initio} molecular dynamics (MD) simulations. The remarkable observation when comparing all the studied liquids is that the rate of increase of \( \gamma \) upon compression is approximately universal. It can be described by \( q = (d\ln \gamma/d\ln V) = -1.5\pm0.25 \) in all seven compositions. This places very strong constraints on microscopic models for silicate liquid compression behavior and suggests a general rule for computing isentropes and densities of silicate liquids of arbitrary composition under any conditions likely to occur in a terrestrial mantle or magma ocean.

Keywords: Silicate liquids, pre-heated experiments, Grüneisen parameter, geophysics.

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INTRODUCTION

Silicate liquids are central agents in physical and chemical evolution of terrestrial planets. Understanding the pathways of such evolution thus requires knowing where and when melting occurs, the fractionation of elements between solid and liquid phases, and the physical properties (e.g., density and viscosity) of the liquids that result. Although melting of silicates in the modern Earth is mostly restricted to pressure \( (P) \leq 3 \) GPa, extending our knowledge of all these properties to \( P \geq 100 \) GPa is motivated both by the likelihood of impact-induced deep magma oceans during Earth accretion and the seismic observation of present-day melting in the boundary layer above the core.

The only methods presently available to study the thermal equation of state (EOS) of liquids under such conditions are shock compression and MD. Both require extrapolation downwards in temperature from measured or calculated states to reach conditions of geophysical interest. Along with the importance of adiabatic temperature profiles in convecting systems like magma oceans, this makes the Grüneisen \( \gamma \) parameter critical:

\[
\gamma = \frac{\left(\frac{\partial P}{\partial E}\right)_V}{\left(\frac{\partial P}{\partial T}\right)_V} = \frac{\gamma_{ak}}{c_r} = \frac{\left(\frac{\partial \ln T}{\partial \ln V}\right)_s}{\left(\frac{\partial P}{\partial T}\right)_V}
\]

(1)

Grüneisen \( \gamma \) is especially convenient for expressing thermal pressure: in many materials it is, to good approximation, a one-parameter function of volume (i.e. independent of temperature or internal energy), which leads directly to the Mie-Grüneisen approximation and EOS.

The general behavior that is observed in crystalline materials is that \( \gamma \) decreases upon...
 compression, often roughly as \((\gamma/V) = \text{constant}\). More generally, a handy (though empirical) form for describing the volume dependence of \(\gamma\) is

\[
\frac{\gamma}{\gamma_o} = \left(\frac{V}{V_o}\right)^q
\]  

(2)

For solids, \(q\) is positive and often close to unity. The origin of changes in \(\gamma\) in crystalline materials is well understood in terms of lattice dynamics and anharmonicity [e.g., 1]. In liquids, however, the physical origin of \(\gamma\), the expected dependence on volume, and the relationship of such dependence to microscopic structure are not understood.

Given the uncertainties in computing \(\gamma\) from shock compression data, it is necessary to sample across a large range in \((V/V_o)\) to constrain \(q\). Thus experiments reaching \(P \geq 100\) GPa have opened this area for investigation.

**SUMMARY OF PUBLISHED RESULTS**

At this time, data reaching sufficient compression to constrain the volume dependence of \(\gamma\) are available for seven compositions.

**SiO₂**

SiO₂ liquid is anomalous in that its thermal expansion coefficient (\(\alpha\)) at ambient \(P\) is taken to be zero. In fact, the temperature derivative of the partial molar volume of SiO₂ in a range of silicate liquids regresses to zero within error [2]. This is the best estimate of \(\alpha\) for pure liquid SiO₂, in the absence of direct determination. This implies (equation (1)) that \(\gamma_o\) is also zero for liquid SiO₂. Thus \(\gamma(V)\) for SiO₂ cannot be expressed in the form of equation (2), but any determination of a positive \(\gamma\) at elevated \(P\) would be consistent with the general behavior of increasing \(\gamma\) upon compression.

Lyzenga et al. [3] determined the Hugoniot and shock temperatures of liquid SiO₂ along the principal Hugoniots of \(\alpha\)-quartz and fused silica. Comparison of these Hugoniots yielded “loosely constrained” values of \(\gamma_o = 1.4, q = +0.5\), based on liquid data covering \(Ps\) 73 to 137 GPa. Independently, liquid sound speed from rarefaction velocity in the same study yielded \(\gamma = 1.6 \pm 0.2\) for liquid SiO₂ at 97.5 GPa. Hence, at least referenced to the ambient \(P\) properties, compression increases the \(\gamma\) of liquid SiO₂.

The offset Hugoniot method, applied to the stishovite segments of each Hugoniot by [3] yielded \(q = +3.2\). This is reasonably consistent with \(q = +2.6\) for stishovite from Luo et al. [4], using Hugoniots of quartz, coesite and stishovite within the stishovite field and also with all available porous silica data in the stishovite regime. Thus, the extraction of negative \(q\) from comparison of offset Hugoniots is specific to liquid-phase data.

**MgSiO₃**

Hugoniot data on MgSiO₃ from initial states including glass, enstatite, porous enstatite, and highly porous oxide mix were assigned to liquid shock states by Mosenfelder et al. [5]. Data cover a large range in internal energy and tightly constrain the value of \(\gamma\) at high \(P\). The best fitting value of \(q\), for ambient properties from [6], is \(-1.71 \pm 0.31\). Although the ab initio MD study of Stixrude and Karaki [7] fitted a linear relation between \(\gamma\) and \((V/V_o)\) \((q = -1)\), the value from that study agrees within error with \(\gamma\) from multiple Hugoniots in the \((V/V_o)\) range occupied by the data. The difference is only in assumed functional dependence of \(\gamma(V)\).

Comparison of Hugoniot points with multiple initial states achieving solid shock states in the Mg-perovskite or post-perovskite structures gave high-\(P\) values of \(\gamma\) for those solids [5]. The analysis yielded decreasing \(\gamma\) upon compression for both solids, showing again that the increase for silicate liquids is a robust feature required by the data.

**Mg₂SiO₄**

The \(\gamma\) for Mg-rich olivine liquid has been determined by two independent methods. Brown et al. [8] measured sound speed in \((\text{Mg}_{0.3}\text{Fe}_{0.1})_2\text{SiO}_4\) olivine shocked to 168 GPa, assigned to liquid phase by the drop in sound speed from lower \(P\) data. This data yielded \(\gamma = 2.1 \pm 0.1\), clearly much larger than the ambient \(P\) value \(\gamma = 0.81\). Mosenfelder et al. [9] reported Hugoniot data for forsterite and wadsleyite including two data points on each Hugoniot assigned to Mg₂SiO₄ liquid. Analysis of these data alone constrained \(\gamma = 2.6 \pm 0.35\) for this liquid in the range 150 to 200 GPa.
This analysis was revised by Mosenfelder et al. [5], who found that a 4th order Birch-Murnaghan isentrope plus Mie-Grüneisen thermal $P$ EOS was able to fit all data on Mg$_2$SiO$_4$ liquid from ambient $P$ to 200 GPa. This fit gave $q = -2.04$, a more moderate increase in $\gamma$ with compression than the original analysis [9]. However, this number contained an error in the estimate of $\gamma_o$; correction of this error yields our current best estimate of $q = -1.47$. With this final revision, the agreement with ab initio MD [10] becomes quite good; both methods unquestionably agree on a substantial increase in $\gamma$ upon compression of Mg$_2$SiO$_4$ liquid.

**Diopside-Anorthite Eutectic**

The minimum-melting composition along the binary CaMgSi$_2$O$_6$-CaAl$_2$Si$_2$O$_8$ is an Fe-free basalt analogue. The value of $\gamma$ at ambient conditions is 0.356 [11]. The value at high $P$ was tightly constrained by Asimow and Ahrens [12] from the combination of several pre-heated liquid Hugoniot data and a single high-precision Hugoniot point on an isochemical room-temperature solid aggregate of diopside and anorthite. The difference between the Hugoniots in $U_s - u_p$ space gives $q = -1.63$. Fitting all the data for this composition to Birch-Murnaghan isentropes gives $-1.784 \geq q \geq -2.059$.

**Fe$_2$SiO$_4$**

Preheated liquid EOS data for Fe$_2$SiO$_4$ and room-temperature single-crystal fayalite data were both reported by Chen et al. [13]. We have extended both data sets with new high-$P$ experiments that confirm the pre-heated liquid Hugoniot of [13] and show that the highest-$P$ data from room-temperature single-crystal fayalite reach the liquid regime. Analysis of the difference between these Hugoniots shows increasing $\gamma$ upon compression of this liquid, $q = -1.46$. Full analysis of these data are forthcoming [14].

**Diopside and Anorthite**

These compositions only have data on the preheated liquid Hugoniot and so constraints on the $\gamma(V)$ for these compositions are weak. Fitting shock wave data for each composition to a Birch-Murnaghan isentrope and Mie-Grüneisen thermal $P$ yields some constraint on $q$, though it suffers from parameter trade-off with $K'$. In both cases, the preferred values are consistent with the other liquids discussed herein: $q = -1.6 \pm 1.0$ for diopside and $-1.71$ for anorthite.
curves are all similar. In all cases $\gamma$ increases by about a factor of 3 as $V$ decreases by a factor of 2.

If $\gamma$ of silicate liquids is related to average coordination number of cations [7], then this universality implies that all 7 liquids have roughly the same relationship between densification and coordination increase. On the other hand, if $\gamma$ of liquids is better explained by configurational entropy and random packing of spheres [15], then the universality suggests similar packing fractions for all the studied liquids. In either case, at this point enough compositions have been studied that we can recommend adoption of $q = -1.5 \pm 0.25$ as a plausible guess for prediction of $\gamma$ at elevated $P$ in any naturally-occurring silicate liquid.

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