Direct shock wave loading of Stishovite to 235 GPa: 
Implications for perovskite stability relative to an 
oxide assemblage at lower mantle conditions

Sheng-Nian Luo,1 J. L. Mosenfelder,2 P. D. Asimow,2 and Thomas J. Ahrens1

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[1] Pure stishovite and coesite samples with zero porosity and dimensions appropriate for planar shock wave experiments have been synthesized with multi-anvil high-pressure techniques. The equation of state of stishovite is obtained by direct shock wave loading up to 235 GPa: \(K_0 = 306 \pm 5\) GPa and \(K'_0 = 5.0 \pm 0.2\) where \(K_0\) and \(K'_0\) are ambient bulk modulus and its pressure derivative, respectively. The Hugoniot (shock equations of state) for stishovite, coesite and quartz achieve widely differing internal energy states at equal volume and therefore allow us to determine the Gruneisen parameter of stishovite. On the basis of the resulting \(P-V-T\) equation of state for stishovite and previous studies on other phases on the MgO-SiO2 binary, the breakdown reaction of MgSiO3-perovskite to MgO and SiO2 was calculated. Our calculations show that perovskite is thermodynamically stable relative to the stishovite and periclase assemblage at lower mantle conditions. We obtain similar results for a range of models, despite the appreciable differences among these experiment-based thermodynamic parameters.


1. Introduction

[2] \(\text{SiO}_2\) is an abundant oxide component of the Earth’s mantle, and its thermochemical and mechanical properties are crucial to our understanding of the Earth’s deep interior. Although \(\text{SiO}_2\) is thought to exist only in compounds with other oxide components in the mantle, the properties of the pure end member are needed to verify the thermodynamic stability of \(\text{SiO}_2\)-bearing phases. The polymorphs of silica have been subject of extensive experimental and theoretical studies with various techniques, including ab initio and molecular dynamics modeling [Karki et al., 1997; Luo et al., 2002] and diamond anvil cell (DAC) [Hemley et al., 2000; Panero et al., 2002; Andraut et al., 1998; Andraut et al., 2002; Ono, 2001] and shock wave experiments [Wackerle, 1962; Al’tshuler et al., 1965; Podurets et al., 1981; Marsh, 1981; Furnish and Ito, 1995]. The high pressure polymorph of silica, stishovite, is particularly important due to its implications for the Earth’s lower mantle, and its possible engineering applications as the hardest oxide known [Leger et al., 1996]. Shock wave loading is a unique tool for studying thermal and mechanical properties in that shock-loaded materials are compressed and heated simultaneously. Thus, the equation of state (EOS) and thermal parameters such as the Gruneisen parameter can be obtained. A previous effort at direct shock wave loading on stishovite [Furnish and Ito, 1995] was undermined by sample impurity and porosity due to the challenges in synthesizing large specimens of stishovite with conventional multi-anvil techniques. Here we report our work on the synthesis and direct shock wave loading of pure polycrystalline stishovite, and the geophysical implications.

2. Static Synthesis and Dynamic Loading of Coesite and Stishovite

[3] To avoid edge effects and ensure accuracy in planar shock wave measurements with streak camera diagnostics (the camera used can record 80–100 ns shock propagation times with ~1% precision), the minimum required dimensions of a disk-shaped sample are ~1 mm in thickness and ~3 mm in diameter. This presents a challenge for the synthesis of stishovite, which requires pressures above ~10 GPa. Typical dimensions of the recovered sample in multi-anvil cells that reach 10 GPa are ~1.5 mm in diameter [Rubie, 1999]. A new technique was adopted to radically simplify the assembly to maximize space: the \(\text{ZrO}_2\) insulator, \(\text{LaCrO}_3\) heater, MgO spacer, and sample capsule typically used in modern multi-anvil experiments were dispensed with and only a Re foil was used as both heating element and sample container. The starting material is a cylinder of pure silica glass. The stishovite samples were synthesized at nominal conditions of 14 GPa and 1000°C using 14 mm sintered MgO octahedra, 8 mm truncation-edge-length tungsten carbide anvils and pyrophyllite gas. The recovered samples are well-shaped cylinders with bulk density \((\rho_0)\) of 4.31 ± 0.04 g/cm³, diameter of ~4 mm and thickness of ~2.5 mm. These samples are pure stishovite with zero porosity as evidenced by density measurement, optical microscopy and X-ray diffraction pattern. The Hugoniot of coesite shocked into the stishovite regime was previously determined up to 112 GPa [Podurets et al., 1981] and can serve as a reference state for measurements on stishovite if verified and extended to higher pressure. Therefore we also synthesized pure coesite samples for shock wave loading with a cubic multi-anvil device at approximately 4 GPa and 900°C. The final bulk density \((\rho_0)\) of these samples is 2.92 ± 0.03 g/cm³. The synthesized coesite and stishovite samples are sectioned into disks of ~1 mm thickness and polished for shock wave experiments. Planar shock wave experiments were conducted on a two-stage light gas gun with projectile velocity \((u_p)\) measured...
results are listed in Table 1. Figure 1 shows the US with the impedance match method [4] on the stishovite Hugoniot. For comparison, it is proposed that a post-stishovite phase exists on the principal quartz and coesite Hugoniot [Akins and Ahrens, 2002]. This could be explained by the temperature differences between quartz (or coesite) and stishovite Hugoniot.

[5] At high pressures, where all three Hugoniots are in the stishovite-type phase, the internal energy and pressure differences at fixed volume allow estimation of the Gruneisen parameter (γ) of stishovite by finite difference, assuming the Mie-Gruneisen equation of state, i.e., γ = F(∂P/∂E)cR, where E is internal energy. The Hugoniots in the stishovite/post-stishovite regime for quartz and coesite are obtained by fitting to the available data (Figure 2). The Gruneisen parameter for stishovite, γ(V), is obtained from the quartz-stishovite and coesite-stishovite Hugoniot pairs. Fitting to yields γ = 0.90 + 0.23γ0, where γ0 is the ambient Gruneisen parameter [Watanabe, 1982]. The functional form of γ(V) follows Anderson [1995] and McQueen [1991]. In the absence of experimental constraints it is common to assume γ = 1. The Gruneisen parameter of stishovite at lower mantle conditions has not previously been determined from experiments. Thus, our result obtained directly from shock wave experiments provides an important constraint on thermodynamic calculations and geotherm modeling [Stacey, 1992]. The Gruneisen parameter of stishovite also allows the determination of the Anderson-Gruneisen parameter as βγ = 6.6 (given K0T determined next),

\[
U_S \text{ (km/s)} = 2.52 + 1.70u_p; \rho_0 = 2.92 \pm 0.03 \text{ g/cm}^3 \tag{1}
\]

and specific volume (V) at shocked states are determined by flash X-rays and shock wave velocity (U_S) by streak camera, from which the particle velocity (u_p), pressure (P) and specific volume (V) at shocked states are determined with the impedance match method [McQueen, 1991]. The results are listed in Table 1. Figure 1 shows the U_S–u_p relationships for coesite and stishovite. The new coesite data are shown as dotted line for stishovite and dashed line for coesite in high pressure regime.

A linear fit to the shock wave data starting from stishovite yields

\[
U_S \text{ (km/s)} = 9.08 + 1.32u_p; \rho_0 = 4.31 \pm 0.04 \text{ g/cm}^3 \tag{2}
\]

Hugoniots centered at stishovite, coesite and quartz are shown in Figure 2 (the fused quartz data are scattered and not included). Although post-stishovite phases could have formed on the stishovite principal Hugoniot, we observed no direct evidence for such a transition. This could be due to the pressure range over which we conducted the experiments, sluggish kinetics at low shock temperature resulting from the low compressibility of stishovite, or the relatively small changes in structure and energy attending phase transition. In other words, it could be stishovite or post-stishovite phase on the stishovite Hugoniot. For comparison, it is proposed that a post-stishovite phase exists on the principal quartz and coesite Hugoniot [Akins and Ahrens, 2002]. This could be explained by the temperature differences between quartz (or coesite) and stishovite Hugoniot.

<table>
<thead>
<tr>
<th>Shot #</th>
<th>Flyer-driver material</th>
<th>u_p (km/s)</th>
<th>\rho_0 (g/cm^3)</th>
<th>U_S (km/s)</th>
<th>u_p (km/s)</th>
<th>P (GPa)</th>
<th>\rho (g/cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>329</td>
<td>Ta</td>
<td>6.18</td>
<td>4.33</td>
<td>13.89(15)</td>
<td>3.92(1)</td>
<td>235.7(2.4)</td>
<td>6.0(10)</td>
</tr>
<tr>
<td>331</td>
<td>Al1100</td>
<td>5.73</td>
<td>4.26</td>
<td>11.63(12)</td>
<td>2.06(1)</td>
<td>102.2(1.2)</td>
<td>5.18(5)</td>
</tr>
<tr>
<td>332</td>
<td>Ta</td>
<td>4.84</td>
<td>4.32</td>
<td>12.76(14)</td>
<td>3.05(1)</td>
<td>168.1(1.7)</td>
<td>5.67(8)</td>
</tr>
<tr>
<td>333</td>
<td>Ta</td>
<td>5.36</td>
<td>4.30</td>
<td>13.30(14)</td>
<td>3.38(1)</td>
<td>193.6(2.0)</td>
<td>5.76(9)</td>
</tr>
</tbody>
</table>

Numbers in parentheses denote uncertainties in the last 1 or 2 digits.

Figure 1. Planar shock wave experiments on coesite and stishovite. Stishovite experiments were conducted at high pressures above the Hugoniot elastic limit. The U_S–u_p relationships are shown as dotted line for stishovite and dashed line for coesite in high pressure regime.

Figure 2. Shock wave data of silica in P–V space. Quartz data are from [Wackerle, 1962; Al'tshuler et al., 1965; Marsh, 1981]. Hugoniots for quartz, coesite and stishovite have initial density of 2.65, 2.92 and 4.31 g/cm^3 respectively.
all these data sets are in reasonable agreement (Figure 3). Given the uncertainties in pressure calibration in DAC and GPa, the data have been revised and reinterpreted along appreciably denser and softer stishovite EOS up to 120

\[ \text{McQueen}, 1991 \], given our new value for the Gruneisen parameter. Figure 3 shows the 300 K isotherm obtained by jointly fitting the corrected shock wave data and recent lower pressure DAC data [Hemley et al., 2000; Panero et al., 2002; Andrault et al., 2002] to the Vinet equation of state [Vinet et al., 1989]. The fit yields \( K_{OT} = 306 \pm 5 \text{ GPa} \) and \( K_{VT} = 5.0 \pm 0.2 \) in the range of 0–250 GPa, comparable to previous studies at lower pressures [Panero et al., 2002; Andrault et al., 2002; Li et al., 1996]. Although a previous study on stishovite [Andrault et al., 1998] proposed an appreciably denser and softer stishovite EOS up to 120 GPa, the data have been revised and reinterpreted along with the new data below 60 GPa [Andrault et al., 2002]. Given the uncertainties in pressure calibration in DAC and those in volume determination in shock wave experiments, all these data sets are in reasonable agreement (Figure 3).

3. Discussion and Conclusion

The breakdown of MgSiO₃-perovskite at lower mantle conditions has been a subject of extensive investigation and debate [Meade et al., 1995; Saxena et al., 1996; Serghiou et al., 1998; Mao et al., 1997; Shim et al., 2001]. We tackled this issue based on the Gibbs free energy of perovskite relative to that of the assemblage of periclase and stishovite. As previous studies did not predict dramatic structural and energetic changes of perovskite and stishovite under lower mantle conditions, we assume that perovskite as well as stishovite can be described with a single set of EOS and thermodynamic parameters. Our new results for stishovite, along with recent studies on MgSiO₃-perovskite [Saxena et al., 1999], allow a more precise calculation of phase equilibria of the perovskite (denoted as \( \text{Pv} \)), periclase (Pe) and stishovite (St) system, i.e., the Gibbs free energy and volume of the reaction

\[
\text{MgSiO}_3(\text{Pv}) \leftrightarrow \text{MgO}(\text{Pe}) + \text{SiO}_2(\text{St})
\]

The thermodynamic parameters we used are from Fei et al. [1990] and Fei [1995] unless stated otherwise. Using our new results on stishovite and a recent study on MgSiO₃-perovskite [model 1 in Saxena et al., 1999] (denoted as Model 1), we computed the Gibbs free energy and specific volume for each phase at 300–3700 K and 0–150 GPa, from which the Gibbs free energy and volume of reactions (\( \Delta G \) and \( \Delta V \) respectively) were obtained. We adopted a widely-used method to compute these reactions [e.g., Song and Ahrens, 1997]. Figure 4a shows that for 300–3700 K isotherms, perovskite has lower Gibbs free energy than the assemblage of stishovite and periclase at pressures higher than 25–31.5 GPa. Thus for any reasonable geotherm [Brown and Shankland, 1981], perovskite is thermodynamically stable relative to the assemblage of stishovite and periclase at lower mantle pressures. Besides the lower Gibbs free energy, perovskite also has smaller molar volume than the Pe-St assemblage by 0.5 cm³/mol (Figure 4b), i.e., perovskite is about 2% denser than its oxide counterparts at lower mantle conditions. This implies that the relative stability of MgSiO₃-perovskite increases to higher pressures.

To explore the sensitivity of this calculation to the choice of thermodynamic parameters, we conducted similar calculations with alternative parameters for St and Pv. The parameters of Model 2 (i.e., not using our EOS and \( b_T \) for stishovite) from Fei et al. [1990] and Fei [1995] yielded results as shown in Figure 4c–4d. We conclude that Pv is stable with respect to the assemblage of St and Pe. We also examined Model 3 [Andrault et al., 1998 for St and Fei et al., 1990 for Pv], Model 4 (this work for St and Fei et al., 1990 for Pv) and Model 5 (this work for St and model 2 in Saxena et al., 1999 for Pv). All these models predict similar results. This is significant if we consider the appreciable differences among

\[
\Delta G = \frac{1}{C_1} T^3 \left[ \frac{2}{3} K_0 + \frac{1}{2} \frac{K_{OT}}{T} \right] V + \frac{1}{C_2} T^4 \left[ \frac{1}{2} \frac{K_{OT}}{T} + \frac{1}{3} \frac{K_{VT}}{T} \right] V^2
\]

\[
\Delta V = \frac{1}{C_1} T^3 \left[ \frac{2}{3} K_0 + \frac{1}{2} \frac{K_{OT}}{T} \right] V + \frac{1}{C_2} T^4 \left[ \frac{1}{2} \frac{K_{OT}}{T} + \frac{1}{3} \frac{K_{VT}}{T} \right] V^2
\]

\[
\text{Figure 4.} \quad \text{Gibbs free energy and volume of reaction } \text{Pv} = \text{Pe} + \text{St} \text{ for Model 1 (a, b) and Model 2 (c, d).}
\]
the parameters in the reported different models, such as \( K_o, K_A, L_T, \delta_T \), thermal expansivity and specific heat, e.g., for stishovite, \( K_T \) varies from 291 to 314 GPa and \( K_{0-T} \) from 4.3 to 6. Although it was shown that the decomposition of perovskite is possible if the EOS parameters of stishovite are chosen specifically to obtain this result with \( K_{0-T} < 3.5 \) [Pankov et al., 1996], the present experimental results exclude this possibility. Our calculations apply strictly only to the rutile structure of SiO\(_2\) and orthorhombic structure of MgSiO\(_3\) at depths of 670–2300 km [Ono, 2001; Shim et al., 2001], but a large \( \Delta G \) accumulates over their stability regime. Hence, although both stishovite [Hemley et al., 2000; Andraut et al., 2002] and perovskite [Shim et al., 2001] phases may invert to slightly denser forms in the lowermost mantle, we do not expect the oxides to become stable relative to MgSiO\(_3\) phases within the mantle pressure regime (i.e., up to 136 GPa).

[8] Detailed investigation of the stability of perovskite relative to the oxide assemblage in the real lower mantle requires consideration of the influence of other components; most importantly Fe, FeO, CaO and Al\(_2\)O\(_3\). CaO enters the lower mantle except at the core-mantle boundary.

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S.-N. Luo, J. L. Mosenfelder, F. D. Asimow, and T. J. Ahrens, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA. (sluo@gps.caltech.edu)