

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

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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: $K_{0T} = 306 \pm 5$ GPa and $K'_{0T} = 5.0 \pm 0.2$ where K_{0T} and K'_{0T} 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. *INDEX TERMS:* 3944 Mineral Physics: Shock wave experiments; 3939 Mineral Physics: Physical thermodynamics; 3919 Mineral Physics: Equations of state

1. Introduction

[2] SiO₂ 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 SiO₂ 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 SiO₂-bearing phases. The polymorphs of silica have been the 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 ZrO₂ insulator, LaCrO₃ 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 gaskets. The recovered samples are well-shaped cylinders with bulk density (ρ_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 (ρ_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_{fp}) measured

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Table 1. Shock Wave Experiments Parameters

Shot #	Flyer-driver material	u_p (km/s)	ρ_0 (g/cm ³)	U_s (km/s)	u_p (km/s)	P (GPa)	ρ (g/cm ³)
<i>Stishovite</i>							
329	Ta	6.18	4.33	13.89(15)	3.92(1)	235.7(2.4)	6.03(10)
331	Al1100	5.73	4.26	11.63(12)	2.06(1)	102.2(1.2)	5.18(5)
332	Ta	4.84	4.32	12.76(14)	3.05(1)	168.1(1.7)	5.67(8)
333	Ta	5.36	4.30	13.30(14)	3.38(1)	193.6(2.0)	5.76(9)
<i>Coesite</i>							
325	Ta	4.99	2.94	8.90(9)	3.78(1)	98.8(1.0)	5.10(11)
329	Ta	6.18	2.91	10.37(12)	4.61(1)	139.3(1.4)	5.24(13)
331	Al1100	5.73	2.94	7.62(7)	2.99(1)	67.0(0.6)	4.84(9)
332	Ta	4.84	2.92	8.82(9)	3.66(1)	94.4(1.0)	4.99(10)

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

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 in agreement with the previous study [Podurets et al., 1981]. A linear fit to both coesite data sets in the high pressure (stishovite or post-stishovite) regime gives

$$U_s \text{ (km/s)} = 2.52 + 1.70u_p; \rho_0 = 2.92 \pm 0.03 \text{ g/cm}^3 \quad (1)$$

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

$$U_s \text{ (km/s)} = 9.08 + 1.23u_p; \rho_0 = 4.31 \pm 0.04 \text{ g/cm}^3 \quad (2)$$

[4] Hugoniot 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.

[5] At high pressures, where all three Hugoniot 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., $\gamma = V(\partial P/\partial E)_V$, where E is internal energy. The Hugoniot 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, $\gamma(V)$, is obtained from the quartz-stishovite and coesite-stishovite Hugoniot pairs. Fitting to

$$\gamma = \gamma_0(V/V_0)^q; \gamma_0 = 1.35 \quad (3)$$

yields $q = 2.6 \pm 0.2$, where V_0 is the ambient specific volume and γ_0 the ambient Gruneisen parameter [Watanabe, 1982]. The functional form of $\gamma(V)$ follows Anderson [1995] and McQueen [1991]. In the absence of experimental constraints it is common to assume $q = 1$. 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 $\delta_T = 6.6$ (given K'_{0T} determined next),

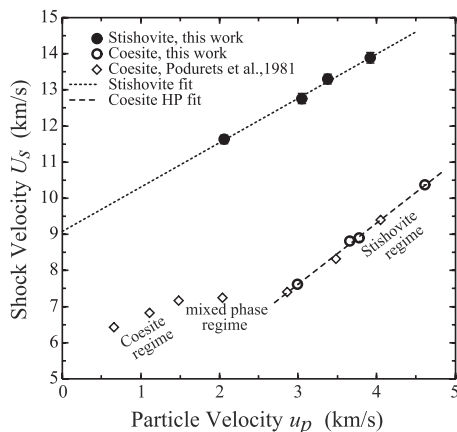


Figure 1. Planar shock wave experiments on coesite and stishovite. Stishovite experiments were conducted at high pressures above the Hugoniot elastic limit. The U_s - u_p relationships are shown as dotted line for stishovite and dashed line for coesite in high pressure regime.

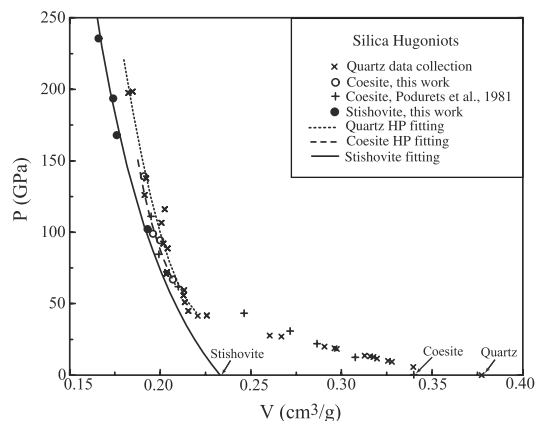


Figure 2. Shock wave data of silica in P - V space. Quartz data are from [Wackerle, 1962; Al'tshuler et al., 1965; Marsh, 1981]. Hugoniot for quartz, coesite and stishovite have initial density of 2.65, 2.92 and 4.31 g/cm³ respectively.

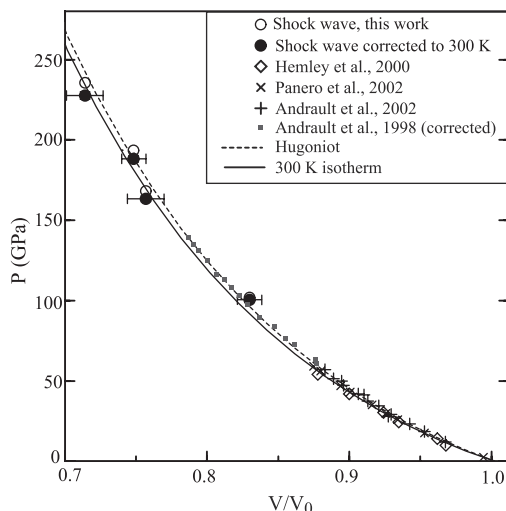


Figure 3. The 300 K isotherm and Hugoniot of stishovite at 0–250 GPa. Solid curve is the Vinet universal EOS fit to the corrected shock wave data and low pressure DAC data at 300k [Hemley *et al.*, 2000; Panero *et al.*, 2002; Andrault *et al.*, 2002]. The data in [Andrault *et al.*, 1998] were corrected in [Andrault *et al.*, 2002]. The shock data points on the Hugoniot and on the isotherm have the same error bars in volume, and the pressure error bars are within the symbol size.

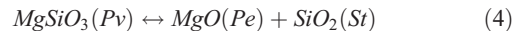
which provides a basis for extrapolation of thermal expansivity of stishovite to high pressures [Anderson, 1995; Birch, 1952].

[6] To construct the equation of state of stishovite to high pressures, we correct the shock wave data to a 300 K isotherm by subtracting the thermal pressure from the shocked state at fixed volume. This pressure correction is obtained by calculating the temperatures along the Hugoniot and the pressure difference between the Hugoniot and 300 K isotherm assuming the Mie-Grüneisen equation of state [McQueen, 1991], given our new value for the Grüneisen 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 $K_{0T} = 306 \pm 5$ GPa and $K'_{0T} = 5.0 \pm 0.2$ 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

[7] 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 Pv), periclase (Pe) and stishovite (St) system, i.e., the Gibbs free energy and volume of the reaction



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 (ΔG and ΔV 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.

[8] 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 δ_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

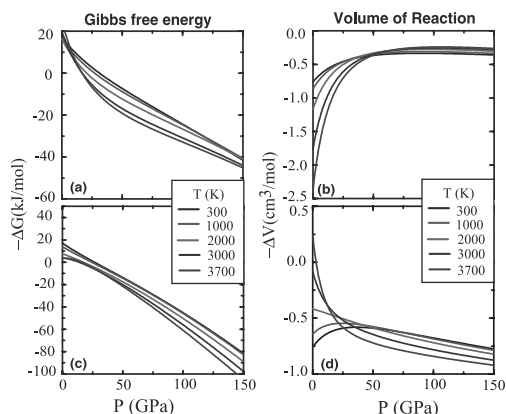


Figure 4. Gibbs free energy and volume of reaction Pv = Pe + St for Model 1 (a, b) and Model 2 (c, d).

the parameters in the reported different models, such as K_0 , K'_{0T} , δ_T , thermal expansivity and specific heat, e.g., for stishovite, K_T varies from 291 to 314 GPa and K'_{0T} 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 $K'_{0T} < 3.5$ [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 ΔG accumulates over their stability regime. Hence, although both stishovite [Hemley *et al.*, 2000; Andrault *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).

[9] 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_2O_3 . CaO enters the separate phase Ca-perovskite. Al_2O_3 substitutes into Mg-perovskite and expands its stability field relative to Pe and St. Although FeO substitutes into both Pe and Pv and can shift the equilibrium either way, a recent study did not observe different behavior of $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3$ perovskite at lower mantle conditions [Shim *et al.*, 2001]. At the core-mantle boundary (as opposed to within the bulk of the lower mantle), the involvement of metallic Fe in the reaction of (Mg, Fe)-perovskite, magnesiowustite and stishovite-type phases could induce the decomposition of (Mg, Fe)-perovskite to mixed oxides and the sequestration of Fe into the outer core [Song and Ahrens, 1994]. These reactions could be expected to contribute to the anomalous seismic observations in the D'' region [Knittle and Jeanloz, 1991]. In natural multicomponent assemblages, however, stishovite and its higher pressure CaCl_2 and $\alpha\text{-PbO}_2$ forms remain essentially pure SiO_2 , so experiments on the EOS and thermal properties of SiO_2 remain directly relevant to calculating stability relations in the presence of other components. Unless experiments reveal dramatically different thermochemical and mechanical parameters for the poorly known higher pressure polymorphs, we expect the thermodynamic stability of perovskite or its related structures relative to the oxide assemblage through the lower mantle except at the core-mantle boundary.

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