A Proposed Equation of State of Stishovite

Thomas J. Ahrens, Taro Takahashi, and Geoffrey F. Davies

The available shock-wave data for solid α quartz in the stishovite pressure regime are reduced to a 25°C isotherm and an adiabat, centered at standard conditions, using recent standard density, enthalpy, and coefficient of thermal expansion data. The calculated iso-
thermal bulk modulus, 3 Mb, as determined from the Birch-Murnaghan equation, depends critically on the value of (dK/dP), at zero pressure and to a yet unknown extent on the form of the equation of state. The high-temperature value of Grüneisen's ratio (0.8 to 0.9) along the α quartz (stishovite regime) Hugoniot was obtained from the pressure offsets of the fused quartz and porous quartz Hugoniot. The high value for γ obtained from thermo-
chemical data at standard conditions (1.5 ± 0.3) suggests that a marked decrease in the value of γ to 0.8 occurs with increasing temperature.

INTRODUCTION

The reduction of the shock-wave (Hugoniot) data for stishovite to adiabats and isotherms depends critically on the value of the thermo-
dynamic Grüneisen parameter γ and its variation with volume and perhaps temperature, as well as the analytic form of the assumed equa-
tion of state. In earlier analyses [McQueen et al., 1963; Anderson and Kanamori, 1968; Ahrens et al., 1969], a temperature-independent γ (i.e. Mie-Grüneisen assumption) and a volume-
dependent γ, specified only by the longitudinal vibrational contribution to the lattice anhar-
monicity, have been assumed. Determinations of γ that take no account of the acoustic shear or optic lattice modes may be in serious error [Anderson, 1968]. The consideration of only longitudinal acoustic vibrations may also be in error in some cases, such as for stishovite, where the Hugoniot data extend from temperatures below to temperatures above the Debye temperature.

In the present analysis we employ only thermodynamic values of the Grüneisen parameter, determined at zero and high pressure,
in the form of an empirical relation specifying γ along the Hugoniot.

Since ultrasonic and complete thermochemical data for stishovite are not yet available, we assume a two-parameter (Birch-Murnaghan) pressure-density curve for the raw Hugoniot, 25°C isotherm and adiabat centered at standard conditions. We note that for solids, such as stishovite, for which the pressure-density curves of interest remain in the regime below or pass through the Debye temperature (~1100°C), the validity of the Mie-Grüneisen assumption may be also be questioned. Thomsen and Anderson [1969] have recently demonstrated that the isothermal Birch-Murnaghan equation and the Mie-Grüneisen assumption are not consistent with lattice dynamics in the anharmonic high-
temperature approximation. To the extent that the high-temperature data for α quartz and fused quartz have been fitted to pressure-
density curves of the Birch-Murnaghan form, and γ is assumed to be a function of only volume at high temperature, the present analy-
sis suffers from this inconsistency. The degree to which the use of the Birch-Murnaghan form affects the present results, particularly in deter-
mining the higher-order parameter such as (dK*/dP), is not clearly understood.

Shock-wave equation-of-state data for stishovite were first obtained (inadvertently) by Wackerle [1962] in his study of α quartz and fused quartz. Using the value of 4.35 g/cm³ for the zero-pressure density of stishovite reported by Stishov and Popova [1961] and the shock data for SiO₂ above 400 kb, McQueen et al. [1963] estimated the quartz to stishovite trans-

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formation energy \((1.5 \times 10^9 \text{ ergs/g})\), Grüneisen ratio \((0.9)\), and zero-pressure bulk sound speed \((10 \text{ km/sec})\).

Since the study of McQueen et al. [1963], Chao et al. [1962] obtained a refined value of stishovite density, \(4.287 \text{ g/cm}^3\), by means of X-ray diffraction study of natural polycrystalline stishovite. New shock data for stishovite have also been obtained by Al'tshuler et al. [1965] in the form of three new Hugoniot points extending to nearly 2 Mb. Hugoniot data for a porous aggregate of quartz (sandstone) Jones et al. [1968], and new data obtained for fused quartz by H. Shipman (private communication, 1969) and by McQueen and his associates [McQueen, 1968] have also become available. In addition, the enthalpy and heat capacity have been determined by Holm et al. [1967], and the thermal expansion by J. S. Weaver (private communication, 1969). It has now become possible to calculate the thermodynamic Grüneisen parameter at high temperature and high pressure and to analyze the high-pressure shock-wave for \(\alpha\) quartz with fewer assumptions than in previous treatments.

**ANALYSIS**

As discussed above, the raw Hugoniot data for shocked quartz above 400 kb are represented in analytic form by the Birch-Murnaghan equation of the form

\[
p_n = \frac{3}{2} K_{0n} \left[ \left( \frac{p}{p_0} \right)^{7/3} - \left( \frac{p}{p_0} \right)^{5/3} \right] - \left( 1 - 3 \left( 1 - K_{0n}/4 \right) \left( \frac{p}{p_0} \right)^{2/3} - 1 \right)
\]

where \(p_n\) is pressure, \(p\) and \(p_0\) are density at pressure \(p\) and zero-pressure, and \(K_{0n}\) and \(K'_{0n}\) are the zero-pressure bulk modulus and \((\partial K_{0n}/\partial p)_n\) along the raw Hugoniot, the adiabat centered at standard conditions, or the 25°C isotherm. The subscript \(n\) indicates either the raw Hugoniot, \(n = h\), and adiabat \(n = a\), or the 25°C isotherm, \(n = t\). The parameter \((\partial K_{0n}/\partial P)_n\) or \(K''_{0n}\) is negative and is fixed by the form of equation 1. The shock-wave and auxiliary thermodynamic data are used to calculate the parameters \(K_{0n}\) and \(K'_{0n}\) (Table 1) from the empirically determined dependence of \(\gamma\) along the Hugoniot. The value of these parameters will depend on the fact that we have chosen a pressure-volume curve of the Birch-Murnaghan form. Recently, L. Thomsen (unpublished data, 1969) has derived a high-temperature fourth-order equation of state in which the volume dependence of the Grüneisen parameter and \(K''_{0n}\) are self-consistently related. The application of the present data to Thomsen's fourth-order equation centered at an appropriate high temperature remains to be carried out.

The data of Wackerle [1962] in the range 414 to 725 kb and those of Al'tshuler et al. [1965] at pressures of 595, 887, and 1974 kb are combined. We note that in Al'tshuler et al., Table 1, the density for the data point at 887 kb is listed as being 4.695 g/cm³. The measured shock-wave parameters indicated in the table, when combined with the Rankine-Hugoniot equations give a high-pressure density of 4.904 g/cm³. This value was assumed since it is self-consistent with the other data.

By taking specific volume, \(v = 1/p\), as the independent variable and \(p_n\), the pressure along

<table>
<thead>
<tr>
<th>TABLE 1. Equation-of-State Parameters for Stishovite</th>
</tr>
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<tbody>
<tr>
<td>Solution</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
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<tr>
<td>4</td>
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<tr>
<td>5</td>
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<tr>
<td>...</td>
</tr>
</tbody>
</table>

* Calculated from \(\gamma_0 C_{0s}/K_{0s}\).

* (apparent zero-pressure bulk modulus along \(\alpha\) quartz Hugoniot \((K_{0h})\) for apparent density of 4.26 g/cm³.

* (\(dK_{0s}/dp\))₈.
TABLE 2. Birch-Murnaghan Parameters, 25°C Isotherm Stishovite from X-ray Data

<table>
<thead>
<tr>
<th>$K_{01}$, mb</th>
<th>$K_{01}$, mb</th>
<th>$(dK_{01}/dP)_{T}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.23 ± 0.1</td>
<td>2.62 ± 0.3</td>
<td>8.0</td>
</tr>
<tr>
<td>3.31</td>
<td>2.69</td>
<td>6.0</td>
</tr>
<tr>
<td>3.40</td>
<td>2.76</td>
<td>4.0</td>
</tr>
<tr>
<td>3.49</td>
<td>2.83</td>
<td>2.0</td>
</tr>
<tr>
<td>3.54</td>
<td>2.87</td>
<td>1.0</td>
</tr>
<tr>
<td>3.59</td>
<td>2.92</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*Liu et al. [1969].
*Bassett and Barnett [1969].

the Hugoniot, as the dependent variable, the pressure $p_{a}$ along the stishovite adiabat centered at standard conditions, is calculated from Ahrens et al. [1969]:

\[ p_{a}(v_{s} - v) = -\int_{v_{o}}^{v_{s}} (p_{a} \, dv) + \int_{p_{a}}^{p_{s}} (v/\gamma) \, dp + \Delta \varepsilon, \quad (2) \]

where $v_{o}$ is the initial volume of quartz, 0.3776 cm$^{3}$/g, $v_{s}$ is the initial volume of stishovite, 0.2333 cm$^{3}$/g, $\gamma$ is the thermodynamic Gr"uneisen ratio

\[ \gamma = \frac{\nu(\partial p/\partial \varepsilon)_{s}}{\alpha K_{s}/c_{p} \rho_{s}} \quad (3) \]

and $\Delta \varepsilon$, is the internal energy of transformation for the reaction quartz $\rightarrow$ stishovite under standard conditions, 0.821 $\times$ 10$^{6}$ ergs/g [Holm et al., 1967]. The variation of $\gamma$ along the Hugoniot at temperatures between 25°C isotherm and the Hugoniot is given empirically by equation 4. Here $\alpha$, $K_{s}$, and $c_{p}$ have their usual meaning. The Gr"uneisen ratio under standard conditions was obtained by calculating $K_{s}$ by integrating equation 2 and applying equation 3 where $\alpha = (15 \pm 2) \times 10^{-6}$ °K$^{-1}$ (J. S. Weaver, personal communication, 1969) and $c_{p} = 0.7151$ erg/g °K [Holm et al., 1967]. On the other hand, if we use the zero-pressure isothermal bulk moduli of 2.8 and 3.4 Mb as measured respectively by Bassett and Barnett [1969] and Liu et al. [1969] (see Table 2), we obtain a zero-pressure Gr"uneisen ratio of 1.37 ± 0.18 and 1.66 ± 0.19. Although $\gamma$ is a function of temperature and pressure, an empirical functional form for relating $\gamma$ and volume was used since the temperature effect on $\gamma$ is not clearly understood:

\[ \gamma = \gamma_{0}(v/v_{0})^{A} \quad (4) \]

where $A$ is an adjustable parameter. It should be pointed out that it is not clear whether the variation in $\gamma$ along the Hugoniot specified by equation 4 is consistent with the Birch-Murnaghan equation and the Mie-Gr"uneisen assumption at high temperature.

Because of the relatively high Debye temperature of stishovite, $\gamma$ may depend more strongly on temperature than on volume along the Hugoniot. In order to evaluate $A$, the data for porous and fused quartz are employed to provide an independent determination of $\gamma$ at high pressure. This is discussed in the next section.

The pressure $p_{i}$ along the 25° isotherm is obtained at a series of volumes by eliminating the temperature along the adiabat $T_{a}$ between the following equations:

\[ T_{a} = 298 \int_{p_{a}}^{p_{i}} \gamma \, dv/v \quad (5) \]

\[ p_{i} = p_{a} - \int_{p_{a}}^{p_{i}} (\gamma c_{s} \, dT/v)_{s} \quad (6) \]

where $c_{s}$ is the specific heat at constant volume. The dependence of $c_{s}$ on temperature and volume is assumed to be that of a Debye solid. The Debye temperature $\theta_{D}$ at standard conditions, 1142°K, is calculated from the empirical relation for oxides proposed by Anderson [1965]:

\[ \theta_{D} = 164 \rho_{0}^{4/3} \quad (7) \]

When thermal expansion versus temperature data for stishovite become available, it will be possible to calculate $c_{s}$ from $c_{p}$ versus temperature relation and fit the resulting curve to the Debye formula.

The relation of the high-pressure Hugoniot curve to the calculated adiabat and 25° isotherm is shown in Figure 1, and equation-of-state parameters for stishovite obtained from the reduction of the shock-wave data using a range of values of $\gamma_{0}$ and $A$ (consistent with the data for $\alpha$ and $\gamma$) are given in Table 1. It is seen that the value for $\gamma_{0}$ strongly influences the value of $A$, whereas it affects the value for $K_{0}$ in a lesser degree. Among the five sets of pa-
rameters computed, the parameters in solution 5 are preferred. Although \( \partial \gamma / \partial T \), is probably nonzero in the vicinity of room temperature, it is interesting that the values for \( \partial K_{00}/\partial P \) and \( \partial (K_{00}/\partial T) \), calculated for stishovite are quite close to those measured by Manghnani [1969] and Chung and Simmons [1969] for rutile (Table 3), which is isostructural and has nearly the same density as stishovite. Bassett and Barnett [1969] and Liu et al. [1969] have determined the \( K_{00} \) values for stishovite by fitting their pressure-volume data obtained by X-ray diffraction to the Birch-Murnaghan equation, equation 1. Their value for \( K'_{00} \) \( = (\partial K_{00}/\partial P)_{T=0} \) was set at 4. However, we have observed that the value for \( K_{00} \) thus calculated depends on the choice of the value for \( K'_{00} \), as shown in Table 2. If the value for \( K'_{00} \) is chosen to be 7 (solution 5), the \( K_{00} \) values obtained from the X-ray diffraction data are consistent with the \( K_{00} \) value in the solution 5 of this study.

The use of equation 4, with appropriate parameters for \( \gamma \) and \( A \) to describe the volume or temperature dependence of the Grüniesen ratio along the Hugoniot, rather than the Dugdale-MacDonald relation, has the effect of reducing the zero-pressure bulk modulus from 3.6 Mb given by Ahrens et al. [1969] to \( \sim 3.0 \) Mb and increasing \( \partial (K_{0}/\partial P) \), from \( \sim 3 \) to \( \sim 7 \). We note also that the new values for both the Grüniesen ratio and the zero-pressure density of stishovite results in the lowering of the calculated zero-pressure bulk sound speed from the 10 km/sec value of McQueen et al. [1963] to \( 8.4 \pm 0.2 \) km/sec for the shock data or \( 8.4 \pm 0.6 \) km/sec from high pressure X-ray data.

**GRÜNEISEN'S RATIO AT HIGH PRESSURE**

With the availability of high-pressure Hugoniots data in the stishovite regime for porous aggregates of quartz (actually Coconino sandstone) obtained by Jones et al. [1968], it is possible to apply the thermodynamic definition

### Table 3. Comparison of Elastic and Thermodynamic Data for Stishovite and Rutile

<table>
<thead>
<tr>
<th>Material</th>
<th>( \rho_0 ), g/cm(^2)</th>
<th>( C_p ), ergs/g</th>
<th>( \alpha ), K(^{-1})</th>
<th>( K_{00} ), kb</th>
<th>( \partial K_{00}/\partial P ), ( \partial (K_{00}/\partial T) ), kb/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2) (Stishovite)</td>
<td>4.287</td>
<td>0.715 ( \times 10^7 )</td>
<td>15.0 ( \pm 2.0 ) ( \times 10^{-6} )</td>
<td>2000</td>
<td>7(^*), 5(^\dagger)</td>
</tr>
<tr>
<td>TiO(_2) (Rutile)</td>
<td>4.250(^*)</td>
<td>0.7125 ( \times 10^7 )</td>
<td>22.75 ( \times 10^{-6} )</td>
<td>3370</td>
<td>6.4(^\dagger), 6.76(^\dagger)</td>
</tr>
</tbody>
</table>

\(^*\) Single-crystal value.
\(^\dagger\) Crystal measured by Manghnani [1969].
\(^\dagger\) Holm et al. [1967].
\(^\dagger\) Determined by Weaver (1969, private communication) by means of the X-ray diffraction method in a temperature range of 8\(^\circ\)C to 800\(^\circ\)C using synthetic stishovite.
\(^\dagger\) Analysis of shock data, \( \alpha \) quartz.
\(^\dagger\) Birch-Murnaghan fit of the X-ray data of Liu et al. [1969].

Fig. 1. Pressure-density Hugoniot curves for solid and porous (sandstone) \( \alpha \) quartz and fused quartz in the stishovite regime. Calculated adiabat centered at standard conditions and 25\(^\circ\)C isotherm for stishovite are calculated from solid \( \alpha \) quartz data. Isothermal X-ray data for stishovite compares closely with calculated 25\(^\circ\)C isotherm.
of Grüneisen's ratio (equation 3) to obtain an independent determination of $\gamma$ at high pressure. The Hugoniot data for Coconino sandstone, which has an initial density of $1.98 \text{ g/cm}^3$, are also shown in Figure 1. For a given density these data indicate a higher pressure than the data for stishovite obtained by shocking a quartz. This results because of the greater thermal pressure accompanying compression for the distended (26% porosity) state. In order to calculate Grüneisen's ratio, the internal energies and pressures at a given density are differenced to form the ratio

$$
\gamma = \frac{\gamma_{SS} - \gamma_{QQ}}{(e_{SS} - e_{QQ})} \tag{8}
$$

where the subscripts $SS$ and $QQ$ denote sandstone and quartz. The assumptions implied by equation 8 are:

1. The sandstone is pure quartz. The analysis of Jones et al. [1968] indicates 97% quartz and 3% feldspar, with a trace of heavy minerals. Because of the similarity of quartz and feldspar in density and Si-O coordination in both the low- and high-pressure phase (hollandite structure in the case of feldspar, [Ringwood et al., 1967], the effect of the feldspar impurities should be small.

2. The energy required to reduce the porosity of sandstone to zero upon shock compression, plus the surface energy of the quartz grains, is negligible as compared with the shock energy. The compaction energy can be roughly estimated by assuming it to be comparable to the energy required to isothermally collapse the pore structure of sandstone. Assuming a pressure of the order of 50 to 100 kb is required [Stephens and Lilley, 1968], a compaction energy of $\sim 6 \times 10^6 \text{ ergs/g}$ is obtained. The surface energy for quartz grains of 0.5-mm diameter, is $\sim 10^5 \text{ ergs/g}$ [Brace and Walsh, 1962]. The energies are both small compared with the shock energies associated with the densities given in Table 4.

3. For the high-temperature states lying between the quartz and sandstone Hugoniots, Grüneisen’s ratio is only a function of volume (or density). This implies that the finite difference of equation 8 is mathematically equivalent to the derivative in equation 3. A critical test of this assumption would be to compare the apparent Grüneisen’s ratios obtained from Hugoniot data for the same compound with different initial densities. As shown in Table 4, the values of $\gamma$ calculated from the Hugoniot data for solid and fused quartz and sandstone (excluding the region of double-valued density versus pressure) are essentially in agreement with each other. This observation supports the assumption above.

The values of Grüneisen’s ratio obtained from each of the high-pressure data points for sandstone are given in Figure 2 and Table 4. The first four data points give Grüneisen ratios in the density range 4.6 to 4.8 g/cm$^3$ as $0.94 \pm$
0.08. As can be seen from Figure 1, the single point at $p = 4.648 \text{ g/cm}^3$ is associated with a higher pressure than the points at densities of 4.659 and 4.818 g/cm$^3$. If these data are taken at their face value, the pressure along the Hugoniot curve for sandstone appears to become a double-valued function of density above a pressure of approximately 1 Mb [Kormer et al., 1962]. The maximum density achieved along the Hugoniot of a substance may be used to obtain yet another determination of the Grüneisen's ratio at high pressure. For this purpose the Mie-Grüneisen equation is written in the form:

$$p_a - p_a = \left(\frac{\gamma}{\nu}(e_a - e_a)\right)$$  \hspace{1cm} (9)

where the different pressures and energies along two pressure-volume (or density) curves, in this case the Hugoniot and adiabat, are related by the thermodynamic Grüneisen ratio. At the point at which a maximum in the density (or minimum in the volume) occurs $(\partial P_a/\partial V)_h = \infty$ or $(\partial P_a/\partial V)_s = -\infty$. Substituting $e_a$ for $e$, $e_a = p_a - (\nu_{0, a} - \nu)/2$ and differentiating results in

$$[\partial P_a/\partial V]_h = \left[\partial (\gamma/\nu)/\partial (\nu_{0, a} - \nu)\right][1 - (\gamma/2)(\nu_{0, s} - \nu)]$$

$$- [p_a - (\gamma/\nu)(e_a - e_a)]$$

$$\cdot [(1/2)(\partial \gamma/\partial (\nu_{0, a} - \nu_{0, s}))/2(\partial (\gamma/\nu)/\partial \nu)]$$

$$\cdot [1 - (\gamma/2)(\nu_{0, s} - \nu) - 1]^{-2}$$  \hspace{1cm} (10)

where $e_a$, the energy along the adiabat of stishovite, relative to $\alpha$ quartz at standard conditions, is given by

$$e_a = - \int_{v_{0, a}}^{v_{0, s}} p_a \, dv + \Delta e_a = e_a + \Delta e_a$$  \hspace{1cm} (11)

Equation 10 then yields

$$\gamma[\partial P_a/\partial V]_h = 2(\nu_{0, s} - 1)^{-1}$$  \hspace{1cm} (12)

provided that

$$[\partial P_a - (\gamma/\nu)(e_a - \Delta e_a)]$$

$$\cdot [(\partial \gamma/\partial (\nu_{0, a} - \nu_{0, s})) - \nu_{0, s}(\partial (\gamma/\nu)/\partial \nu)] \neq 0$$

Estimating the density interval in which the slope of the pressure-density Hugoniot approaches $+\infty$ as 4.65 to 4.82 g/cm$^3$, equation 12 yields upon substitution of these densities the values of Grüneisen's ratio in the range of 1.49 to 1.40. We note that the values for $\gamma$ at these densities are nearly 1.5 times as great as those calculated by equation 8. Since the sandstone Hugoniot represents far higher temperature conditions from those for fused quartz and solid quartz, the Grüneisen ratios calculated from equation 12 may represent the thermodynamic properties of the liquid.

The method outlined by McQueen et al. [1963] is also used to calculate the Grüneisen ratio of stishovite from the recent shock data for fused quartz (Table 4). As can be seen in Figure 2, the value of $\gamma$ of 0.9 obtained by McQueen et al. [1963] is quite compatible with the present results but only at high pressure. The curve $\gamma = 1.58 (\rho/p)^{1/2}$ shown in Figure 2 corresponds to solution 5 of Table 1.

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