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High-pressure crystal chemistry of stishovite

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ABSTRACT

A high-pressure single-crystal X-ray diffraction study of stishovite, the highest pressure polymorph of SiO_2 known, has been completed to 16 GPa. The compressibility of stishovite is anisotropic with **a** approximately twice as compressible as **c**. Consequently, the axial ratio *c/a* increases with pressure. The observed unit-cell compression gives an isothermal bulk modulus of 313 GPa using a Birch-Murnaghan equation of state. With increasing pressure, the primary structural response is the compression of the Si-O bonds and O···O separations. Neither the O-Si-O angle nor Si-O-Si angles show a significant change with pressure. The longer axial Si-O bonds are more compressible than the shorter equatorial Si-O bonds. Among the O···O separations, O(1)···O(1) (i.e., the *c* axis) is least compressible, followed by the O(1)···O(2) separation, the shared octahedral edge, and lastly by the O(1)···O(3) separation. The incompressibility of the O(1)···O(1) separation can be explained by the nature of the strong Si···Si repulsive forces across the shared octahedral edge. Moreover, the decrease in the O(1)···O(2) separation, which is the shared octahedral edge, increases the shielding between the Si atoms. The SiO_6 octahedra in stishovite show no change in distortion with increasing pressure. The polyhedral bulk modulus of SiO_6 is 342 GPa, the largest known value among octahedral units of rutile-type oxides.

INTRODUCTION

Stishovite is the highest pressure polymorph of SiO_2 known, and is stable at pressures in excess of 10 GPa. Stishovite possesses the rutile structure with each Si atom bonded to six O atoms in an octahedral configuration and each O atom bonded to three Si atoms. The high density of stishovite, 4.29 g/cm³, is approximately 46% greater than that of coesite, the densest of the silica polymorphs with tetrahedrally coordinated Si, and is achieved mainly by increasing the coordination of Si from four to six.

Structural studies of stishovite at high pressure have direct relevance to geophysical and mineralogical studies of the Earth's mantle. Stishovite is expected to be the form of any free silica in this region, produced either by transformation of α quartz or as a disproportionation product of common silicate minerals. Furthermore, octahedral coordination of Si by O has been observed in a number of other high-pressure structure types, including hollandite (Ringwood et al., 1967), wadeite (Kinomura et al., 1975), garnet (Ringwood and Major, 1971), pyroxene (Angel et al., 1988), ilmenite (Kawai et al., 1974), and perovskite (Liu, 1974).

The first high-pressure X-ray studies of stishovite were based on powdered samples and determined the isothermal compression in a solid medium (e.g., Ida et al., 1967; Bassett and Barnett, 1970; Liu et al., 1974) and isothermal compression in a fluid medium (Olinger, 1976; Sato, 1977). These methods provided information about the isothermal bulk modulus and axial compressibilities of stishovite. Unlike the earlier studies, however, the studies of compression in a fluid medium should have been free of any nonhydrostatic stresses. With the breakthrough in synthesizing high-quality single crystals of stishovite, a precise determination of the structure was carried out with single-crystal data (Sinclair and Ringwood, 1978; Hill et al., 1983) and the single-crystal elastic moduli of stishovite were determined from Brillouin scattering experiments (Weidner et al., 1982). Recently, Sugiyama et al. (1987) reported a single-crystal X-ray diffraction study of stishovite to 6 GPa. They found that the shared octahedral edge was more compressible than the unshared edges and the longer Si-O bonds were less compressible than the shorter Si-O bonds. In addition, the polyhedral bulk modulus of the SiO_6 octahedron, 250 GPa, was less than the isothermal bulk modulus, 313 GPa.

In this study, we report results from high-pressure X-ray diffraction experiments on single crystals of stishovite to 16 GPa, nearly tripling the previous range under which stishovite has been studied. The results include determinations of the axial compressibilities, the isothermal bulk modulus and its derivative with respect to pressure, the polyhedral bulk modulus of the SiO_6 octahedron,

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TABLE 1. Unit-cell parameters, axial ratio *c/a*, and unit-cell volume of stishovite between 0 and 16 GPa

P (GPa)	*a* (Å)	*c* (Å)	*c/a*	Vol. (Å³)
0.0001*	4.1797(2)	2.6669(1)	0.63806(6)	46.591(1)
		Crystal #1		
0.0001	4.1801(6)	2.6678(6)	0.6382(2)	46.615(16)
0.7	4.1771(10)	2.6673(8)	0.6386(2)	46.539(25)
1.7	4.1713(11)	2.6655(8)	0.6390(2)	46.378(27)
2.5	4.1667(7)	2.6645(6)	0.6395(2)	46.260(18)
3.1	4.1638(9)	2.6622(8)	0.6394(2)	46.155(24)
4.0	4.1593(6)	2.6613(5)	0.6398(2)	46.041(16)
4.5	4.1563(9)	2.6603(7)	0.6401(2)	45.956(24)
		Crystal #2		
3.2	4.1627(9)	2.6629(7)	0.6397(2)	46.143(24)
4.7	4.1560(8)	2.6601(8)	0.6401(2)	45.946(21)
6.5	4.1481(8)	2.6558(8)	0.6403(2)	45.697(22)
9.0	4.1337(10)	2.6517(7)	0.6415(2)	45.312(25)
15.0	4.1043(12)	2.6417(10)	0.6436(3)	44.500(29)
		Crystal #3		
2.5	4.1670(10)	2.6628(6)	0.6390(2)	46.237(24)
7.7	4.1394(8)	2.6538(8)	0.6411(2)	45.471(20)
11.0	4.1246(7)	2.6474(6)	0.6419(2)	45.039(19)
13.1	4.1141(9)	2.6443(6)	0.6427(2)	44.757(21)
15.8	4.1023(9)	2.6402(6)	0.6436(2)	44.432(21)

* Sugiyama et al. (1987).

and the structural compression mechanism operative in stishovite. These results are compared with the 1987 study of Sugiyama et al. In addition, the high-pressure behavior of stishovite is compared with that of other rutile-type oxides.

EXPERIMENTAL

The synthetically grown stishovite crystals used in this study were synthesized at 1650 °C and 15 GPa using a uniaxial split-sphere apparatus (USA-2000) at the Stony Brook High-Pressure Laboratory. The crystals of stishovite were by-products of experiments in which a sodium pyroxene phase with six-coordinated Si was synthesized (Angel et al., 1988). Details of the experimental conditions are given in Gasparik (1989). Suitable stishovite crystals were chosen on the basis of optical examination and precession photographs. The crystals that were mounted in the gas cell, which were necessarily required to be very small, were examined on a RIGAKU AFC-5 diffractometer equipped with a rotating anode generator. For both crystals, the lattice parameters measured from a set of high-angle reflections showed good agreement with those reported by Sinclair and Ringwood (1978) [$a = 4.1772(7)$ Å and $c = 2.6651(4)$ Å] and those reported by Hill et al. (1983) [$a = 4.1773(1)$ Å and $c = 2.6655(1)$ Å]. In addition, results from room-pressure refinements on intensity data collected outside the diamond-anvil cell for the crystals used in this study were in excellent agreement with the results of Sinclair and Ringwood (1978) and Hill et al. (1983).

The first crystal, an 80 × 70 × 25 μm plate flattened on (110), was mounted in a triangular Merrill-Bassett type diamond-anvil cell (Hazen and Finger, 1977) with an Inconel 750X gasket (350 μm-diameter hole). The stishovite crystal and several 10 to 15 μm Cr^{3+}-doped ruby chips were affixed to one diamond face with a thin smear of the alcohol-insoluble fraction of vaseline. The pressure-transmitting medium was a 4:1 mixture of methanol to ethanol. Procedural details of crystal mounting, pressure calibration, and cell operation are given in Hazen and Finger (1982).

Unit-cell parameters were obtained at 0.7, 1.7, 2.5, 3.1, 4.0, and 4.5 GPa as well as room pressure. At each pressure from 10 to 12 reflections with $20° \leq 2\theta \leq 34°$ were centered at eight equivalent positions, following the procedure of King and Finger (1979). Initial unit-cell refinements were made without constraints (i.e., as triclinic) to test for deviations from tetragonal dimensionality. All unit-cell angles at all pressures were 90° within two estimated standard deviations, and *a* was within two estimated standard deviations (esd) of *b*. Final cell parameters, recorded in Table 1, were determined by the vector least-squares method with tetragonal constraints (Ralph and Finger, 1982). Full sets of intensity data were collected at 0.0, 1.7, 2.5, and 4.0 GPa.

A fragment of the first crystal measuring 40 × 35 × 25 μm was selected for study in a diamond-anvil cell designed by Mao and Bell (1980) that uses solidified gas as the pressure medium (Mills et al. 1980; Jephcoat et al. 1987). This four-screw cell, which features opposite pairs of screws oppositely threaded for uniform pressurization, is suitable for X-ray diffraction studies of single crystals to above 20 GPa (Hazen and Finger, 1982). The stishovite crystal and ruby chips were mounted against one diamond face and enclosed by an indented Inconel gasket with a 200-μm hole. We placed the cell, slightly opened, in a steel pressure vessel, which was pressurized to 0.2 GPa with neon gas. The diamond cell is sealed by a remote-controlled motorized gear assembly, and cell operation then proceeds in the normal manner.

Unit-cell parameters were obtained at 3.2, 4.7, 6.5, 9.0, and 15.0 GPa using 10 to 12 reflections with $20° \leq 2\theta \leq 34°$ (Table 1). The scattering intensity from crystals in high-pressure gas-cell studies is drastically reduced because of the need to use tiny crystals (to be able to attain the high pressures and prevent crushing) and the increased X-ray absorption from the reinforced components of the cell. In this study, the strongest reflections from the crystal were approximately 50 counts per second. Intensity data were collected using steps of 0.025° in omega scans, counting 20 seconds per step, at 4.7, 9.0, and 15.0 GPa. Upon applying pressure in excess of 15 GPa, the crystal fractured.

An effort was made to collect data at pressures in excess of 15 GPa by mounting a crystal 35 × 33 × 18 μm in the gas cell with neon as the pressure medium. The crystal was oriented with the (111) plane parallel to the diamond face. Angular measurements for unit-cell determinations were obtained at 2.5, 7.7, 11.0, 13.1, and 15.8 GPa from 10 to 12 reflections with $20° \leq 2\theta \leq 34°$ (Table 1). Complete sets of intensity data were obtained at 2.5 GPa and 11.0 GPa using 0.025° steps and 20 second-per-step

TABLE 2. Summary of refinement conditions and pressure dependence of the O positional parameter and isotropic temperature factors of Si and O

P (GPa)	Independent obs. reflections	R (%)	R_w (%)	x_O	B_O	B_{Si}
0.0001*	236	1.5	—	0.3062(1)	0.234(5)	0.152(4)
0.0001**	209	1.5	1.8	0.30613(7)	0.245(6)	0.172(5)
0.0001†	27	1.4	1.0	0.3067(3)	0.31(5)	0.15(3)
1.7	24	2.8	1.4	0.3065(5)	0.39(8)	0.14(4)
2.5	35	2.6	1.6	0.3061(5)	0.22(6)	0.29(3)
4.0	30	2.8	1.1	0.3063(4)	0.39(6)	0.12(3)
4.7	22	3.0	1.7	0.3062(8)	0.15(12)	0.05(7)
9.0	26	3.5	2.1	0.3057(9)	0.09(12)	0.13(7)
11.0	23	4.3	3.3	0.3057(16)	0.46(20)	0.17(12)
15.0	24	3.4	1.7	0.3053(10)	0.46(12)	−0.05(6)

Note: Numbers given in parenthesis are esd of last figure cited.
* Sinclair and Ringwood (1978).
** Sugiyama et al. (1987).
† This study, in diamond-anvil cell.

counting times. The O positional parameter determined from refinement of the data collected at 2.5 GPa agreed with that determined from the first crystal at the same pressure (Table 2) within two esd. At 19.4 GPa, the crystal became bridged between the diamond faces resulting in a marked deviation from tetragonal dimensionality with b significantly less than a (i.e., more than 7 esd) and γ more than two esd from 90°. Unfortunately, the peak profiles were too broad for any meaningful refinement to be carried out on this strained crystal.

Monochromatized Mo$K\alpha$ radiation (λ = 0.71069 Å) was used for all the diffraction-intensity measurements. All accessible reflections, including crystallographically equivalent reflections, to $\sin \theta/\lambda \leq 0.7$ were obtained by the ω-scan technique on a Huber four-circle diffractometer equipped with a conventional sealed X-ray source. Corrections were made for Lp effects and absorption by the components of the diamond-anvil cell. No correction was made for absorption by the crystal because of the sufficiently small value of the linear absorption coefficient (μ_l = 15.76 cm^{-1}). Refinements were carried out with RFINE4 (Finger and Prince, 1975) applying the robust-resistant weighting method of Prince et al. (1977). The refinements were initiated with the atomic coordinates of Sinclair and Ringwood (1978), and complex scattering factors for neutral atoms were obtained from the *International Tables for X-ray Crystallography* (1974). The refinement conditions and refined structural parameters are recorded in Table 2; a list of the observed and calculated structure factors has been deposited as Table 3.[1] Selected bond lengths and angles are presented in Table 4.

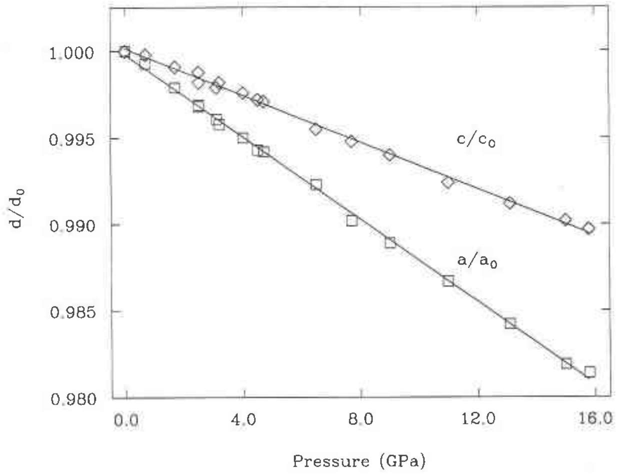

Fig. 1. The variation of a/a_0 (squares) and c/c_0 (diamonds) from 0 to 16 GPa for stishovite crystals used in this study.

RESULTS AND DISCUSSION

Axial compressibilities

The crystals in this study displayed anisotropic behavior as a function of pressure with the a axis approximately twice as compressible as the c axis (Fig. 1). Consequently, the c/a axial ratio increases with increasing pressure (Table 1). The axial compressibilities calculated from linear regressions of the lattice parameters versus pressure are $\beta_a = 1.19 \times 10^{-3}$ GPa^{-1} and $\beta_c = 0.68 \times 10^{-3}$ GPa^{-1} (Table 1). These values are in excellent agreement with the results of Sugiyama et al. (1987) and are consistent with the powder diffraction work of Olinger (1976) and Sato (1977) (Table 5). The axial compressibilities differ slightly from the Brillouin scattering results of Weidner et al. (1982): β_c is slightly, but not significantly, larger than the acoustic value, whereas β_a is 0.13×10^{-3} GPa^{-1} less than the acoustic value (Table 5). However, axial compressibilities calculated from the single-crystal elastic moduli essentially determine the slope of the a versus P or c versus P curve at zero pressure. A better comparison between the two methods can therefore be made by using only the lattice parameters determined at low pressures from X-ray diffraction to evaluate β_a and β_c. If only the data between 0 and 5 GPa are used to calculate β_a and β_c for stishovite, values of 1.28×10^{-3} GPa^{-1} and 0.65×10^{-3} GPa^{-1} are obtained, which are in much better agreement with the acoustic values of 1.32×10^{-3} GPa^{-1} and 0.60×10^{-3} GPa^{-1}, respectively.

The difference in a and c axial compressibilities can be explained, in large part, in terms of the cation-cation and anion-anion electrostatic interactions across and along the shared edges between the SiO_6 octahedra. In stishovite, the effect of Si···Si repulsion across the shared edge (i.e., parallel to **c**) is minimized by shortening the shared edge between the octahedra [i.e., the O(1)···O(2) separation in Fig. 3], resulting in a shielding effect that reduces the repulsive forces between the Si atoms. Indeed, the

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[1] A copy of Table 3 may be ordered as Document AM-90-433 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 4. Selected interatomic distances and angles, octahedral volumes, and distortion indices of SiO_6 octahedra as a function of pressure

Pressure (GPa)	Si-O(1) [4]* (Å)	Si-O(3) [2] (Å)	O(1)-O(2) [2] (Å)	O(1)-O(3) [8] (Å)	O(1)-O(1) [2] (Å)	O(1)-Si-O(2) (°)	Si-O(3)-Si (°)	Octa. vol. (Å³)	Quad.** elon.	Angle** vari.
0.0001†	1.7572(1)	1.8087(2)	2.2903(2)	2.5217(1)	2.6655(1)	81.34(1)	130.67(1)	7.3609(7)	1.00805(3)	27.3
0.0001‡	1.7582(2)	1.8095(3)	2.2919(6)	2.5230(1)	2.6669(1)	81.35(2)	130.68(1)	7.373(1)	1.00803(4)	27.3
0.0001§	1.7564(6)	1.8130(10)	2.285(2)	2.5243(5)	2.6678(6)	81.17(5)	130.58(2)	7.369(6)	1.0084(2)	28.4
1.7	1.7548(12)	1.8081(18)	2.283(4)	2.5196(9)	2.6655(8)	81.16(9)	130.58(4)	7.335(10)	1.0084(3)	28.4
2.5	1.7554(9)	1.8032(14)	2.286(3)	2.5166(7)	2.6645(6)	81.26(7)	130.63(4)	7.321(11)	1.0082(4)	28.0
4.0	1.7519(9)	1.8016(13)	2.279(3)	2.5129(8)	2.6613(5)	81.15(6)	130.57(3)	7.284(7)	1.0084(3)	28.6
4.7	1.7512(15)	1.8000(22)	2.278(4)	2.5113(12)	2.6603(7)	81.15(11)	130.57(6)	7.272(15)	1.0084(5)	28.5
9.0	1.7458(17)	1.7873(26)	2.271(5)	2.4984(14)	2.6517(7)	81.17(13)	130.58(7)	7.176(16)	1.0083(6)	28.6
11.0	1.7428(30)	1.7829(47)	2.267(9)	2.4932(25)	2.6474(6)	81.16(23)	130.58(12)	7.134(27)	1.0083(10)	28.5
15.0	1.7383(19)	1.7721(28)	2.260(6)	2.4824(15)	2.6417(10)	81.10(14)	130.55(7)	7.035(17)	1.0083(6)	28.7

* Bracketed figures represent bond multiplicity.

** Quadratic elongation and angle variance are distortion parameters defined by Robinson et al. (1971). Values for regular polyhedra are 1.0 and 0.0, respectively.

† Hill et al. (1983).

‡ Sugiyama et al. (1987).

§ This study, in diamond-anvil cell.

O(1)···O(2) distance of 2.29 Å observed in stishovite ranks among the shortest of known nonbonded O···O separations (Shannon, 1976). Furthermore, Hill et al. (1983) observed significant bridges of electron density between the maxima along the Si-O(1) and Si-O(2) bonds, thus providing evidence of the shielding effect between the Si atoms. With increasing pressure, the structure is most incompressible along **c** because of the repulsive forces between the Si atoms in the edge-sharing octahedra of the structure.

Table 6 presents a comparison of the axial compressibilities of stishovite with rutile, TiO_2, and the rutile-type oxides, GeO_2 and SnO_2, determined from acoustic measurements and single-crystal X-ray diffraction studies. Similar to stishovite, **a** is approximately twice as compressible as **c** in each of these compounds. Stishovite is the least compressible, followed by GeO_2, and then by SnO_2 and TiO_2, which are very similar. Thus c/a increases with increasing pressure in all of these compounds. In contrast to their similar behavior with pressure, these compounds exhibit quite different behavior with increasing temperature. Rao (1974) reported values for the ratio of thermal expansion coefficients parallel and perpendicular to **c** of 2.1 for GeO_2 and 0.90 for SnO_2. For rutile, TiO_2, the ratio of thermal expansion coefficients of **a** to **c** based on high-temperature data from Meagher and Lager (1979) is 1.4 and for stishovite, using data from Ito et al. (1974a, 1974b) to 600 °C, the ratio is 0.2. Thus, c/a increases with temperature for GeO_2 and TiO_2, decreases slightly with temperature for SnO_2, and decreases sharply with temperature for stishovite. The large variation in high-temperature behavior is evidence that the rutile isomorphs do not conform to the inverse relationship between temperature and pressure whereby the structural variation with increasing pressure is similar to the variation with decreasing temperature (Hazen and Finger, 1982). Hazen and Finger (1981) have suggested that bonding in rutile-type compounds is more covalent than in many other O-based structures and that electrostatic forces may play a smaller role in determining details of the structure, as compared with structures with divalent and monovalent cations. They further point out that bond covalency, nonspherical electron distribution, and metal-metal interactions will change differently with temperature and pressure, thus resulting in violations of the inverse relationship.

TABLE 5. Linear compressibilities of **a** (β_a) and **c** (β_c), the isothermal bulk modulus (K_T) of stishovite and its derivative with respect to pressure (K_T')

β_a ($\times 10^3$ GPa^{-1})	β_c ($\times 10^3$ GPa^{-1})	K_T (GPa)	K_T'	Reference
1.19	0.69	313 ± 4	1.7 ± 0.6	This study
		287 ± 2	6	
		306	2.8 ± 0.2	
1.22	0.64	313 ± 4	6	Sugiyama et al. (1987)
1.32	0.60	306 ± 4	—	Weidner et al. (1982)
1.31	0.57	288 ± 13*	6 ± 1*	Olinger (1976)
		304 ± 14**	1.8 ± 3.1**	
		294 ± 14†	3.2 ± 3.3†	
1.28	0.73	298 ± 5	0.7 ± 1.1	Sato (1977)
		281 ± 2	5	
		294 ± 16**	3.1 ± 3.7**	
		293 ± 8‡	3.7 ± 1.6‡	Bass et al. (1981)

* Value reported by author using an equation of state based on a linear U_SU_P relation.

** Value deduced by Bass et al. (1981) from same data using a Birch-Murnaghan equation of state.

† Value analyzed by Bass et al. (1981) using a Birch-Murnaghan equation of state and modified pressure scale of the NaF standard.

‡ Analysis of combination of Olinger's (1976) and Sato's (1977) data, using a Birch-Murnaghan equation of state and modified NaF pressure scale.

Bulk Modulus and d*K*/d*P*

The pressure dependence of the unit-cell volume is given in Table 1, and the variation of V/V_0 with pressure is shown in Figure 2. The results from this experiment compare well with results from both the high-pressure single-crystal study of Sugiyama et al. (1987; Fig. 2a) and Olinger's (1976) and Sato's (1977) high-pressure powder diffraction studies (Fig. 2b). The isothermal bulk modulus, K_T, was calculated by fitting a Birch-Murnaghan equation of state to all of the pressure-volume data. Using the data from all three crystals and constraining V/V_0 to be equal to one at room pressure, a value of 313 ± 4 GPa was obtained for K_T and a value of 1.7 ± 0.6 was obtained for the derivative of the bulk modulus with respect to pressure, K'_T. These values are in excellent agreement with the studies of Olinger (1976), Sato (1977), Bass et al. (1981), and Weidner et al. (1982) (Table 5). If K'_T is assumed to be 6, the value common to other rutile oxides, a value of 287 ± 2 GPa is obtained for K_T, which is lower than the value of 313 ± 4 GPa obtained by Sugiyama et al. (1987), when K'_T was assumed to be 6.

Determination of the bulk modulus from compression experiments is hampered by the fact that there are so many free variables in the P-V equation of state (such as K'_T and V_0) and the fact that the compression measured is very small. The acoustic experiments provide a much more reliable value for the bulk modulus, since they measure the elastic moduli directly. Furthermore, Bass et al. (1981) found that when the values of K_T determined from acoustic and compression techniques are consistent, the accuracy and precision of the K'_T determined from the compression data can be significantly improved by constraining K_T to be equal to the acoustic value. We can apply this approach to our data, since the value of K_T obtained from the compression experiments, 313 ± 4 GPa, is consistent with the acoustic value, 306 ± 4 GPa. Constraining K_T to be equal to 306 GPa, a value of 2.8 ± 0.2 is found for K'_T, thus reducing the standard deviation of K'_T by a factor of three from calculations using only the compression data. We conclude from these results that K'_T for stishovite is substantially lower than the values reported for other rutile oxides, TiO_2, SnO_2, and GeO_2, that range from 5.5 to 6.8 (Table 6).

Stishovite crystal structure at high pressure

The result from a refinement using intensity data collected in the diamond-anvil cell at ambient pressure compares well with the results of Sinclair and Ringwood (1978), Hill et al. (1983) and Sugiyama et al. (1987) obtained in air (Tables 2 and 4). The crystal structure of stishovite is shown in Figure 3, and the variation of selected bond lengths and angles with pressure is summarized in Table 4. Stishovite crystallizes with the well-known rutile-type (C4) structure, which can be completely described by the two parameters, the ratio of the cell

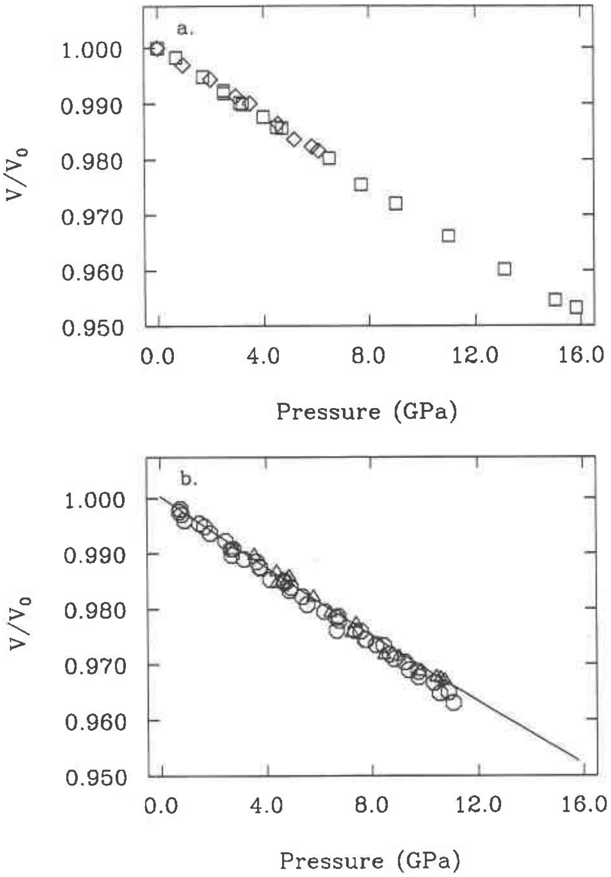

Fig. 2. Comparison of the variation of V/V_0 with pressure for (**a**) single-crystal X-ray diffraction results of this study (squares) and the study by Sugiyama et al. (1987) (diamonds), and (**b**) this study (solid line) with results from the powder X-ray diffraction studies of Olinger (1976) (triangles) and Sato (1977) (circles).

TABLE 6. Comparison of linear axial compressibilities of **a** (β_a) and **c** (β_c), bulk moduli (K) and their derivatives with respect to pressure (dK/dP) for rutile-type oxides

Compound	β_a ($\times10^3$ GPa^{-1})	β_c ($\times10^3$ GPa^{-1})	K* (GPa)	dK/dP	Method of study	Reference
SiO_2	1.19	0.68	313	2.8**	X-ray	This study
	1.32	0.60	306	—	Brillouin	Weidner et al. (1982)
GeO_2	1.52	0.59	258	7†	X-ray	Hazen and Finger (1981)
	1.68	0.62	259†	6.2	Ultrasonic	Wang and Simmons (1973)
SnO_2	1.73	0.78	218	7†	X-ray	Hazen and Finger (1981)
	1.77	0.76	212†	5.5	Ultrasonic	Chang and Graham (1975)
TiO_2	1.80	0.90	216	7‡	X-ray	Hazen and Finger (1981)
	1.94	0.87	214	6.8	Ultrasonic	Manghnani (1969)

* Unless otherwise stated, isothermal bulk moduli and their derivatives with respect to pressure are presented.
** Value obtained by constraining K_T to Brillouin value of 306 GPa (details in text).
† Assumed value used in calculation of K_T from Birch-Murnaghan equation of state.
‡ Isotropic adiabatic bulk modulus, derived from the Voigt-Reuss-Hill approximation.

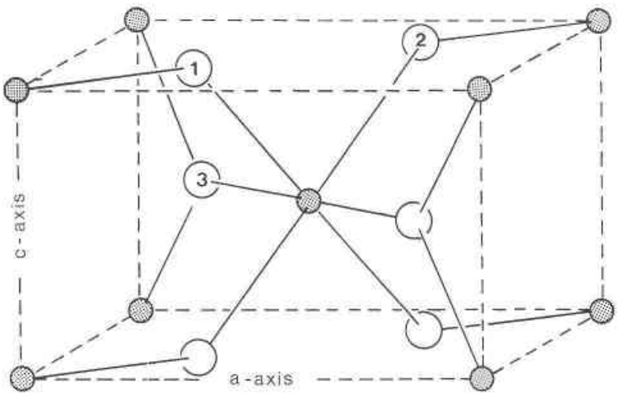

Fig. 3. One unit cell of the stishovite crystal structure at ambient conditions, with atoms labeled that are referred to in the text.

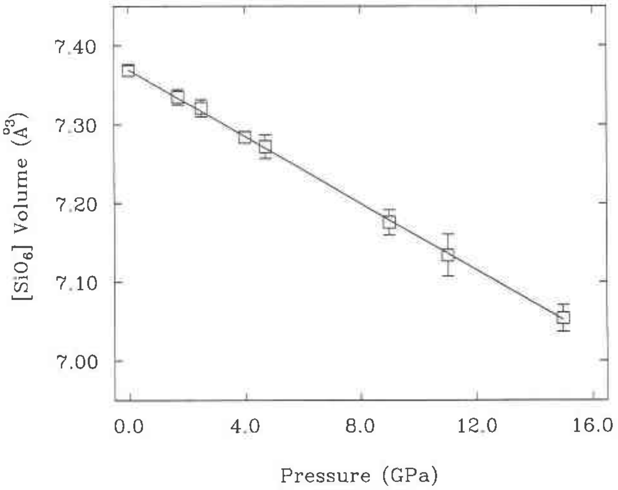

Fig. 4. The volume of the SiO_6 octahedron as a function of pressure.

edges, *c*/*a*, and the single anion positional parameter, x. The SiO_6 unit is not a regular octahedron. The angles subtended by the shared octahedral edge are 81° rather than 90°, and the four Si-O bonds in the (110) equatorial plane of the central octahedron are some 0.05 Å shorter than the two longer axial bonds, which is opposite to the relationship predicted by an ionic model (Baur, 1961; Baur and Khan, 1971). In addition, the nonbonded O···O separation in the shared edge (2.29 Å) is one of the shortest O···O separations known and is considerably shorter than twice the traditional ionic radius of O, 2.64–2.80 Å (Shannon, 1976).

In the previous section, we noted that *c*/*a* increases with increasing pressure owing to the greater compressibility of **a**. The x parameter of O, however, does not show any significant variation with pressure (Table 2), which is similar to results from high-pressure studies on other rutile-type oxides (Hazen and Finger, 1981). From 0 to 6 GPa, Sugiyama et al. (1987) observed a slight increase in the x coordinate of O, although the variation was not greater than three esd.

As mentioned above, the SiO_6 octahedron in stishovite is not a regular polyhedron at ambient conditions. The quadratic elongation and angle variance of the SiO_6 unit, which are both measures of distortion from a regular polyhedron as defined by Robinson et al. (1971), deviate from the ideal values of 1.0 and 0.0, respectively, for a regular octahedron (Table 4). With increasing pressure, no significant change in either of these distortion indices is observed; the quadratic elongation remains within one esd of 1.0084, and the angle variance shows little change from its room-pressure value of 28.4 (Table 4). The angle subtended by the shared octahedral edge, the O(1)-Si-O(2) angle, does not show any significant variation with pressure, and neither does the interoctahedral Si-O(3)-Si angle (Table 4). Sugiyama et al. (1987) found that there is a slight increase in the distortion of the SiO_6 octahedron with increasing pressure, as evidenced by the increase in the quadratic elongation and the decrease in the O(1)-Si-O(2) angle from 81.35° at room pressure to 80.1° at 6.09 GPa. They found that the Si-O-Si angle decreases slightly with pressure, but the decrease is not significant, being less than two esd from the room-pressure value.

The volume of the SiO_6 octahedron decreases almost linearly with increasing pressure (Fig. 4). The polyhedral bulk modulus obtained by fitting a Birch-Murnaghan equation of state to the data is 342 GPa, which is the largest value yet known among the rutile-type oxides. The bulk moduli of the octahedral units of GeO_2, SnO_2, and TiO_2, for comparison, are 270 GPa, 230 GPa, and 220 GPa, respectively (Hazen and Finger, 1982). Thus the trend in the polyhedral bulk moduli closely follows that of the bulk moduli, with stishovite being the least compressible of the rutile-type oxides, followed by GeO_2, and then by SnO_2 and rutile, which both have very similar bulk moduli (Table 6). Moreover, the polyhedral bulk moduli typically have values greater than or equal to the bulk moduli of the entire structure. In the high-pressure study of stishovite by Sugiyama et al. (1987), it was also found that the volume of the SiO_6 octahedron decreases linearly with pressure. However, they calculated a value of 250 GPa for the polyhedral bulk modulus of the SiO_6 octahedron from a Birch-Murnaghan equation of state, which is considerably smaller than both our value and the value of 313 GPa that was found for the bulk modulus of stishovite.

The effect of pressure on the structure is manifest in the compression of the Si-O bonds and O···O separations of the SiO_6 octahedra, shown in Figures 5 and 6, respectively. We observe an approximately linear decrease in the Si-O bond lengths and O···O separations with increasing pressure. The longer axial Si-O bonds (Fig. 5a) are approximately twice as compressible as the shorter equatorial Si-O bonds (Fig. 5b) with bond-length compressibilities calculated from linear regressions of 1.51×10^{-3} GPa^{-1} and 0.70×10^{-3} GPa^{-1}, respectively. Among

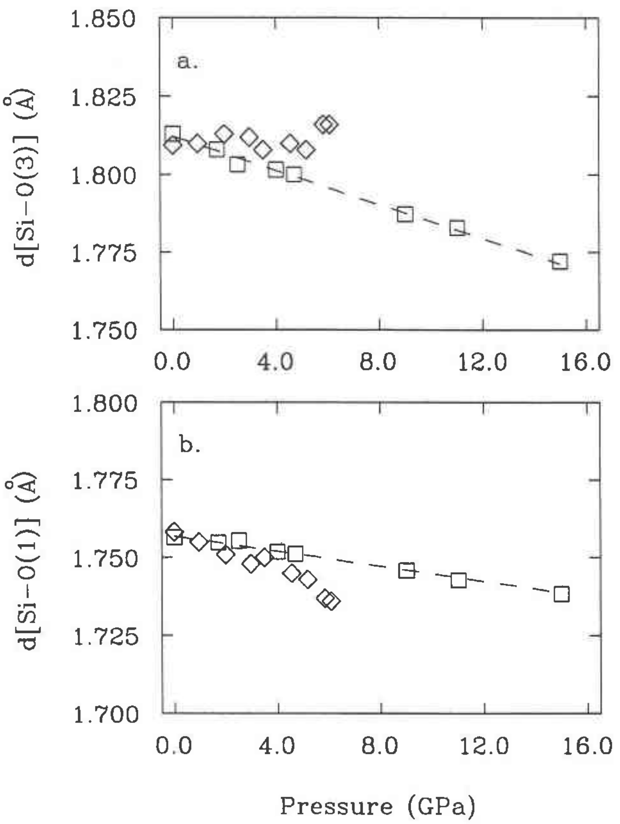

Fig. 5. The Si-O distances of the SiO_6 octahedron as a function of pressure: (**a**) compression of the axial Si-O(3) bonds, and (**b**) compression of the equatorial Si-O(1) bonds. Results from this study are represented by squares and results from the study by Sugiyama et al. (1987) are represented by diamonds.

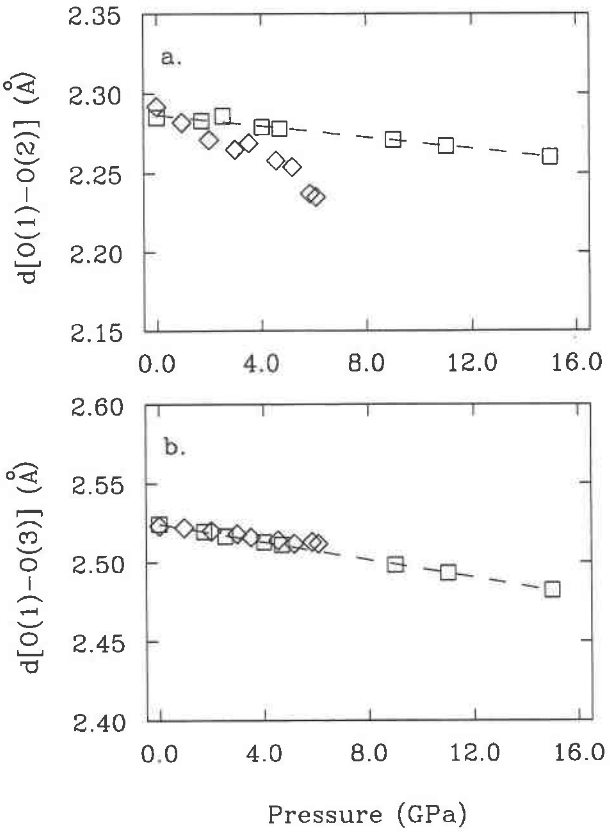

Fig. 6. The O···O separations of the SiO_6 octahedron as a function of pressure: (**a**) variation of the shared octahedral edge with pressure and (**b**) variation of the O(1)···O(3) separation with pressure. Results from this study are represented by squares and results from the study by Sugiyama et al. (1987) are represented by diamonds. The change in the O(1)···O(1) separation (i.e., *c* axis) is presented in Fig. 1.

the O···O separations, the least compressible is the O(1)···O(1) separation, or *c* axis ($\beta_{O1\cdots O1} = 0.68 \times 10^{-3}$ GPa^{-1}), followed by the O(1)···O(2) separation, the shared octahedral edge ($\beta_{O1\cdots O2} = 0.74 \times 10^{-3}$ GPa^{-1}), whereas the O(1)···O(3) separation is the most compressible ($\beta_{O1\cdots O3} = 1.09 \times 10^{-3}$ GPa^{-1} (Fig. 6). Similar to the results of this study, Sugiyama et al. (1987) found that the O(1)···O(1), O(1)···O(2) and O(1)···O(3) distances decrease steadily with pressure and that the *c* axis, O(1)···O(1), is the least compressible O···O separation. However, they found that the shared octahedral edge is more compressible than the O(1)···O(3) separation. In addition, comparison of the results for compression of the Si-O bonds differ between the two studies. Sugiyama et al. (1987) found that the shorter Si-O(1) bonds are more compressible than the longer Si-O(3) bond lengths, which showed a slight increase with pressure.

In the comparison of the results of this study with those of Sugiyama et al. (1987), it must be realized that stishovite is a very incompressible structure and that we are trying to detect subtle, very slight changes in the structure. Thus especial care must be taken in using similar procedures in the collection and analysis of intensity data, since single-crystal diamond-anvil cell experiments are subject to a number of systematic errors. For example, only about a third of reciprocal space is accessible, so any data set is initially biased, with crystallographic and structural parameters perpendicular to the diamond faces less well constrained than those parallel to the faces. Other problems intrinsic to a diamond-cell experiment include nonuniform absorption by Be and diamond components of the cell, shielding of off-center crystals by the X-ray opaque gasket, and the possible crystal deformation due to nonhydrostatic pressure media. These difficulties can be recognized, and for the most part eliminated, by always determining the crystal's room-pressure unit-cell parameters and structure in the diamond-anvil cell. These reference unit-cell and structure data must be obtained using the same experimental conditions as those used at high pressure. In addition, the amount of data accessible in a diamond-anvil cell experiment can be increased by using modified data collection procedures. Finger and King (1978), for example, showed that the fixed-ϕ mode of data collection enhances the number of reflections observed. Changes can also be made in data collection procedures to counteract the effects of the extra material in the beam. The interference from the Be may be avoided by using ω scans rather than conventional θ-2θ scans (Hazen and Finger, 1982).

Both this study and that of Sugiyama et al. (1987) measured unit-cell data at room pressure in the diamond-anvil cell. However, the two studies differed in certain aspects of the data collection procedures. We collected intensity data inside the diamond-anvil cell at room pressure, whereas Sugiyama et al. (1987) collected data outside the cell. They did, however, carry out a refinement at room pressure using the set of reflections that were accessible in the diamond-anvil cell and found that the O positional parameter varied only by 0.00018 between the refinement using all 209 reflections and the one with 26 reflections. Sugiyama et al. (1987) collected intensity data with θ-2θ scans whereas we used ω scans. If one looks more closely at the results from both studies, one finds that the agreement between the two is actually rather good to 5 GPa. There are slight differences in the bond lengths and angles determined at room pressure (Table 3) that might be due to the difference in conditions of collection of intensity data in the diamond cell (this study) as opposed to collection of data in air (Sugiyama et al. 1987). The greatest deviation between the study by Sugiyama et al. (1987) and the present study, however, are the data points at 5.84 and 6.09 GPa from Sugiyama et al. that not only fall off the trends observed in this study, but also deviate from their own trends (Figs. 5 and 6). If one ignores those two points, the agreement between the trends observed in the bond lengths with pressure in the two studies is reasonable (Figs. 5 and 6). Moreover, between 0 and 5.2 GPa, Sugiyama et al. (1987) observe no significant change in the O(1)-Si-O(2) angle or the Si-O-Si angle, similar to this study. There is no significant increase in the distortion of the SiO_6 octahedron between 0 and 5.2 GPa, which is also in agreement with the present study. Finally, the determination of the polyhedral bulk modulus is very sensitive to the last two high-pressure data points. The polyhedral bulk modulus of SiO_6 is closer to 300 GPa if the high-pressure data points at 5.84 and 6.09 GPa are excluded from the calculation. We believe there may have been a problem with the two data points measured at the highest pressures by Sugiyama et al. (1987). Moreover, our study was aided by the fact that we were able to compress stishovite to pressures of 16 GPa, whereas Sugiyama et al. (1987) were limited to pressures of approximately 6 GPa.

CONCLUSIONS

The conclusions from this study can be summarized as follows:

1. The compression of stishovite is anisotropic with the *a* axis almost twice as compressible as the *c* axis. Consequently, the axial ratio, *c/a*, increases with pressure.

2. The isothermal bulk modulus obtained from 17 pressure-volume data from 0 to 16 GPa is 313 ± 4 GPa and 1.7 ± 0.6 for the derivative of the bulk modulus with respect to pressure. If K_T is constrained to be equal to 306 GPa, the value from Brillouin scattering, a value of 2.8 ± 0.2 is obtained for K'_T, which is substantially lower than K'_T values reported for other rutile-type oxides.

3. With increasing pressure, the primary structural response is the compression of the Si-O bonds and O···O separations. Neither the O-Si-O nor Si-O-Si angles show a significant change with pressure. The longer axial Si-O bonds are more compressible than the shorter equatorial Si-O bonds. Among the O···O separations, the O(1)···O(1) (i.e., the *c* axis) is least compressible, followed by the O(1)···O(2) separation, the shared octahedral edge, and lastly by the O(1)···O(3) separation. The incompressibility of the O(1)···O(1) separation can be explained by the nature of the strong Si···Si repulsive forces across the shared octahedral edge. Moreover, the decrease in the O(1)···O(2) separation, the shared octahedral edge, increases the shielding between the Si atoms.

4. The SiO_6 octahedra in stishovite show no change in distortion with increasing pressure. The polyhedral bulk modulus of SiO_6 is 342 GPa, the largest known value among octahedral units of rutile-type oxides.

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