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Effect of Pressure on the Lattice Parameters of Stishovite

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The effect of pressure up to 223 kbar on the lattice parameters and volume of synthetic stishovite was determined at room temperature by means of X ray diffraction techniques. The zero pressure isothermal bulk modulus was evaluated to be 3.44 ± 0.27 Mbar by means of the least squares fit of the volume data to the Birch-Murnaghan equation assuming the K_0' value in the range 2–7. The compression along the *a* axis ($\Delta a/a_0$) is approximately 1.5 times as great as the compression along the *c* axis ($\Delta c/c_0$): $\Delta c/c_0 = (0.66 \pm 0.24)\, \Delta a/a_0$. Similar relationships have been observed for TiO_2 and GeO_2; both are tetragonal and isostructural with stishovite, ultrasonic techniques being used to measure the elastic constants. It is thus suggested that the effect of pressure on the c/a ratios for oxides with the rutile-type structure is predominantly determined by the geometry of the structure and is independent of the size of the cation. The anisotropic compression for stishovite can be explained in terms of a greater extent of overlapping of the electronic orbits parallel to the *c* axis than of the directions perpendicular to the *c* axis.

On the basis of the rapid rate of increase in the seismic parameter ϕ (bulk modulus/density) in the *C* region of the earth's mantle, Thompson [*Birch,* 1952] first predicted that silica may undergo a phase transformation to a rutilelike crystal structure under mantle conditions. The rutilelike silica was later synthesized by *Stishov and Popova* [1961] at high pressure-temperature conditions. It was subsequently discovered by *Chao et al.* [1962] as a product of shock metamorphism of sandstone caused by a meteorite impact and was named stishovite. Its pressure-temperature stability field has been estimated by *Stishov* [1963] and later determined by *Ostrovsky* [1965, 1967], *Akimoto and Syono* [1969], and *Davies* [1972].

The elastic properties of stishovite have been investigated by a number of workers. *McQueen et al.* [1963] calculated the zero pressure bulk modulus of stishovite to be 4.35 Mbar from the shock Hugoniot data for quartz and fused silica obtained by *Wackerle* [1962], the initial density reported by *Stishov and Popova* [1961], and an estimated value for the energy of transformation from quartz to stishovite. *Anderson and Kanamori* [1968] made a similar analysis of the Hugoniot data with a more refined value for the initial density of stishovite obtained by *Chao et al.* [1962] and estimated the value of the bulk modulus to be 3.9 Mbar. *Ahrens et al.* [1970] reduced the Hugoniot data of *Wackerle* [1962], *Al'tshuler et al.* [1965], *Jones et al.* [1968], and others to a 25°C isotherm by using the quartz-stishovite transformation energy determined by *Holm et al.* [1967] and the thermal expansion determined by J. S. Weaver (personal communication, 1970) and obtained a zero pressure bulk modulus value of 3.0 Mbar and its first pressure derivative value of 7.0. More recently, by incorporating new sets of Hugoniot data that greatly extend the ranges of pressure and initial porosities [*Trunin et al.*, 1971*a, b*], *Davies* [1972] determined a bulk modulus value of 3.5 ± 0.1 Mbar and its first pressure derivative value of 3.3 ± 1 from the data of compression (both shock and static), initial density, thermal expansion, and isochoric specific heat. Compressional and shear velocities of sintered stishovite were measured at pressures up to 10 kbar by *Mizutani et al.* [1972]. The bulk modulus calculated from these velocities is 3.46 ± 0.24 Mbar. However, in a brief report a value of 2.93 Mbar was obtained by *Chung* [1973] by means of ultrasonic technique. The discrepancy is not explained by Chung.

The first attempt to determine the pressure-volume relation and the bulk modulus for stishovite under static conditions was made by *Ida et al.* [1967] with a Drickamer-type X ray diffraction apparatus having pressures up to 130 kbar at room temperature. They obtained a zero pressure bulk modulus of 7 Mbar and reported that the bulk modulus decreases rapidly at pressures greater than about 80 kbar. Using a tetrahedral press equipped with X ray diffraction apparatus, *Bassett and Barnett* [1970] determined the pressure-volume relation up to 85 kbar at room temperature and calculated the bulk modulus for stishovite to be 3.0 ± 0.3 Mbar. They considered the data of *Ida et al.* [1967] probably erroneous owing to the interference of the (111) diffraction line for stishovite with the (220) diffraction line for NaCl, which was used as the internal standard for pressure measurements.

In a brief note *Liu et al.* [1969] reported the effect of pressure on the lattice parameters of stishovite at room temperature up to 200 kbar by means of X ray diffraction using a diamond anvil high-pressure cell. The isothermal bulk modulus at zero pressure was calculated to be 3.44 ± 0.20 Mbar by assuming the value of 4 for the first pressure derivative of the bulk modulus. In this paper we have extended the pressure range to 223 kbar and reported the more detailed compression data of stishovite.

SAMPLE AND EXPERIMENTAL METHOD

The sample of stishovite studied in this work was synthesized at an estimated pressure of 90 kbar and a temperature of 1000°C with a Bridgman anvil-type apparatus. Fine-grained cristobalite prepared by heating silicic acid in air at 1100°C was used as a starting material. After the sample was subjected to high pressure and temperature, the charge and a part of the pyrophyllite sample container were treated with hydrofluoric and nitric acids at 100°C to dryness to remove

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TABLE 1. Lattice Parameters and Molar Volume for Stishovite Reported by Various Investigators at 1 bar and Room Temperature

	a_0, Å	c_0, Å	c_0/a_0	V, cm^3/mole
Chao et al. [1962]	4.1790	2.6649	0.6377	14.016
Ida et al. [1967]	4.178	2.665	0.6379	14.01
Bassett and Barnett [1970]	4.178	2.663	0.6374	14.00
This work	4.180 ±0.002	2.666 ±0.001	0.6378 ±0.0004	14.03 ±0.02

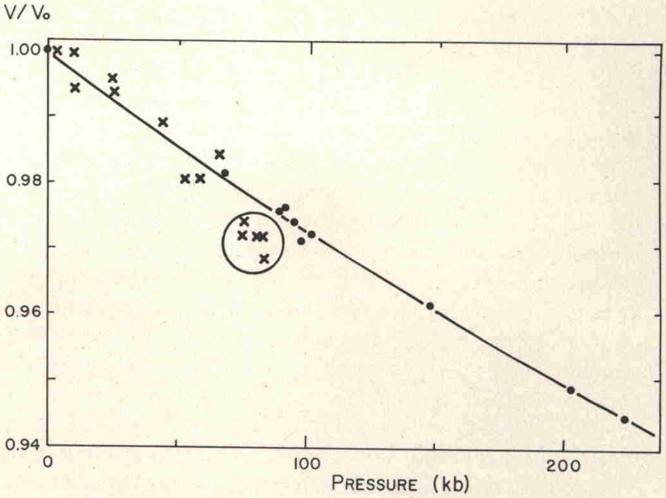

Fig. 1. The pressure dependence of the volume of stishovite at 23° ± 2°C. The solid circles are data points obtained with the diamond press for the present work; the crosses are those obtained with the tetrahedral press [*Bassett and Barnett,* 1970]. The circled cluster is data points believed to have been influenced by deformation of the tetrahedral press. The curve is the plot of the Birch-Murnaghan equation with K_0 = 3350 kbar and K_0' = 5.7.

all the unreacted materials. The treatment was repeated with a hydrofluoric and hydrochloric acid mixture. An examination of the acid-treated sample with the Debye-Scherrer X ray diffraction method indicated that the sample consisted entirely of stishovite and was free of contaminants. Since the sample container was made of pyrophyllite, some part of the stishovite thus obtained may have been a decomposition product of pyrophyllite.

The lattice parameters of stishovite thus synthesized were determined by means of the Debye-Scherrer X ray diffraction method. The values are listed in Table 1 and are also compared with the values published by other investigators. The results of this work agree with others within 0.1%.

A diamond anvil-type X ray diffraction camera developed by *Bassett et al.* [1967] was used in the present study. An intimate mechanical mixture of micron-sized stishovite and NaCl (3 : 1 weight ratio) was compressed between the diamond anvils. Since the highest pressure and the lowest pressure gradients exist at the central area of the sample compressed between the anvils, a finely collimated (60 μm in diameter) monochromatic X ray beam of Mo $K_{\alpha 1}$ was directed to the center of the anvil area. Because of the small size of the sample and the low X ray scattering power of Si and O atoms, exposure times as long as 1000 h were required to produce satisfactory X ray diffraction patterns. These exhibit the diffraction lines (110), (101), (111), (210), (002), and (301) for stishovite and (200) and (220) for the NaCl pressure internal standard. However, the (110) diffraction line for stishovite could not be used for the computation of the lattice parameters because of its superposition with the (200) line produced by an external NaCl platelet placed on the outside surface of the diamond anvil on the film side. This external NaCl was used to monitor the change in camera geometry and film dimension [*Bassett et al.,* 1967]. The lattice parameters for stishovite and NaCl were computed from the diffraction patterns by means of the least squares method. The values for the lattice parameters are accurate to ±0.15%, and hence the volumes calculated from the lattice parameters are accurate to ±0.45%.

The pressures to which stishovite was subjected were calculated from the lattice parameter of the NaCl mixed with stishovite and the pressure-volume relationship for NaCl determined by *Weaver et al.* [1971]. The accuracy of the pressure values reported in this paper has been estimated to be ±2.5%.

EFFECT OF PRESSURE ON VOLUME

The compression data for stishovite up to 223 kbar at room temperature are presented in Figure 1 and Table 2. The zero pressure isothermal bulk modulus K_0 and its pressure derivative K_0' were calculated by a least squares fit of the volume data to the second-order Birch-Murnaghan equation:

$$P = (3/2)K_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}]\{1 - (3/4)(4 - K_0')[(V/V_0)^{-2/3} - 1]\}$$

where V and V_0 are the volumes at pressures P and zero, respectively. The values for K_0 and K_0' thus calculated are K_0

TABLE 2. Experimental Data for Stishovite at 23° ± 3°C

	NaCl			Stishovite					
Run	a, Å	V/V_0	P, kbar	a, Å	c, Å	V/V_0	c/a	$(\Delta a/a_0)$, $\times 10^2$	$(\Delta c/c_0)$, $\times 10^2$
DS-1	5.640	1.000	0	4.180	2.666	1.000	0.6378	0.000	0.000
1LD386	5.308	0.833	68	4.145	2.662	0.982	0.6422	0.844	0.169
1LD387	5.244	0.804	89	4.144	2.648	0.976	0.6390	0.876	0.698
1LD388	5.237	0.800	91.5	4.142	2.651	0.976	0.6400	0.911	0.563
1LD392	5.227	0.796	95	4.145	2.641	0.974	0.6372	0.837	0.971
1LD389	5.221	0.793	98	4.131	2.652	0.971	0.6420	1.182	0.555
1LD390	5.210	0.788	102	4.138	2.646	0.972	0.6394	1.019	0.765
7UP54	5.106	0.742	148	4.119	2.641	0.962	0.6412	1.469	0.945
1LD393	5.006	0.699	202	4.098	2.633	0.949	0.6425	1.959	1.253
1LD394	4.974	0.686	223	4.093	2.628	0.945	0.6421	2.081	1.440

= 3.35 ± 0.05 Mbar and $K_0' = 5.7 \pm 1$. These are in excellent agreement with adiabatic values of $K_0 = 3.35 \pm 0.19$ Mbar and $K_0' = 5.5 \pm 0.6$ reported by *Graham* [1972] in his analysis of Hugoniot data. A substance as incompressible as stishovite, however, does not warrant the procedure that we have followed of fitting the data directly to the Birch-Murnaghan equation to obtain both K_0 and K_0' [*Liu and Bassett,* 1973], and the agreement with Graham's values is certainly fortuitous. This is illustrated by the following analysis. If it is assumed that the stishovite volumes that we measured have no error, we obtain a plot of the sum of residuals $\sum[P_{\mathrm{cal}} - P_{\mathrm{obs}}]^2$ versus K_0' (Figure 2). This plot has a minimum of 5.7. However, if an error of ±0.05% for the measurement of volume is assumed, the relationships shown in Figure 2 clearly indicate that it is impossible to calculate a statistically significant value for K_0' since the error flag is considerably larger than the differences among the residuals for values of $K_0' = 4$, 6, and 8. For this reason, values for K_0 have been calculated for selected values of K_0' (Table 3).

TABLE 3. Initial Isothermal Bulk Modulus for Stishovite at Various Assumed Values of K_0' at 23° ± 3°C

K_0'	K_0, Mbar	Stand. Dev. in K_0, Mbar
2	3.63	0.066
3	3.55	0.056
4	3.47	0.050
5	3.40	0.047
6	3.33	0.046
7	3.26	0.045
8	3.19	0.046

The measured values of K_0' for a number of oxides and silicates fall in the range $K_0' = 4$–6 [*Anderson et al.*, 1968]. On the other hand, the highest and the lowest values of K_0' are 7.0 and 2.1, respectively, evaluated by *Ahrens et al.* [1970] and *Davies* [1972] on the analyses of the shock Hugoniot data of SiO_2. It would be reasonable to assume that the K_0' value for stishovite falls in the range 2–7. The corresponding value of K_0 is 3.44 ± 0.25 Mbar, which includes the range of K_0' values and one standard deviation for the two extreme values of K_0 at K_0' of 2 and 7. The accuracy of the NaCl pressure scale is estimated to be 2.5%, which would cause an additional uncertainty of 0.09 Mbar in K_0 for stishovite. Hence the overall uncertainty for the K_0 value was estimated to be ±0.27 Mbar for stishovite.

Another approach that we can take is to assume that since ultrasonic techniques are considered to yield more reliable elastic moduli, we can fix K_0 at 3.46 ± 0.24 [*Mizutani et al.*, 1972] and use our data to calculate K_0'. In doing so, we have ignored the difference between adiabatic and isothermal conditions, which is small in comparison with the experimental uncertainties. The K_0' value thus obtained is 4.2 ± 3.0, which encompasses the highest and the lowest values of K_0' previously discussed. In a recent study of the elastic constants of a single crystal of GeO_2 with the rutile structure, which is an analog of stishovite, *Wang and Simmons* [1973] felt that the value of K_0' for stishovite should lie between 6 and 7, as the values of K_0' for GeO_2 (rutile) and TiO_2 (rutile) do. On the other hand, however, *Striefler and Barsch* [1973] reported a value of 3.71 for K_0' of stishovite at the Fifty-fourth Annual Meeting of the American Geophysical Union on the basis of their studies of the elastic and optical properties of rutile structure oxides at high pressure. Hence it is our opinion that the value of K_0' for stishovite is still an unresolved matter.

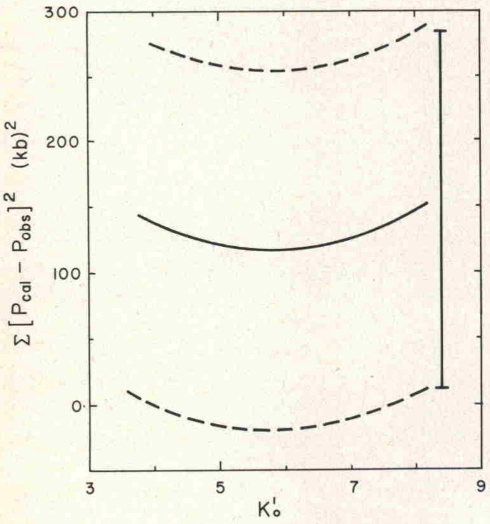

Fig. 2. The solid curve shows the sum of the residuals of the scattering of data points versus the selected values of K_0', when it is assumed that no errors have been made in measuring the volume of stishovite. If an error of ±0.05% for the measurement of volume is assumed, the error flag is much greater than the difference among the residuals for various values of K_0'.

In comparing the present compression data with those obtained by *Bassett and Barnett* [1970], who used a tetrahedral press, it should be noted that the first nine points obtained by the tetrahedral press are in good agreement with the data obtained by the diamond press, and only the last five points are in real disagreement. They cluster below the curve fitted to the present data (see Figure 1). This discrepancy is believed to be the result of deformation of the tetrahedral press once the sample gaskets have essentially ceased to be compressible. Such a deformation changes the sample-detector distance and can introduce a significant error in the measurements of a material as incompressible as stishovite but not in those of samples as compressible as NaCl.

EFFECT OF PRESSURE ON AXIAL RATIO

The effect of pressure on the crystallographic axial ratio c/a is shown in Figure 3. The axial ratio appears to increase linearly by 0.3%/100 kbar, and the relationship can be expressed by

$$c/a = 0.6378 + (2.1 \pm 0.2) \times 10^{-5} P$$

where P is in kilobars.

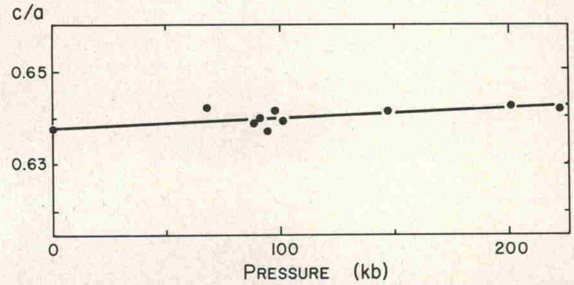

Fig. 3. The pressure dependence of the axial ratio of stishovite. The curve is a plot of the equation $c/a = 0.6378 + (2.1 \pm 0.2) \times 10^{-5}P$, where P is in kilobars. The equation was derived by a least squares fit.

Figure 4 shows a comparison between the linear compressibilities of the *a* axis and the *c* axis. A least squares fit of a linear equation to the data yields a relationship of

$$\Delta c/c_0 = (0.66 \pm 0.24)\ \Delta a/a_0$$

Bassett and Barnett [1970] measured linear compressibilities for stishovite that can be represented by

$$\Delta c/c_0 = (0.4 \pm 0.3)\ \Delta a/a_0$$

The uncertainties for the three equations above denote one standard deviation. The present determination is probably superior to that observed by *Bassett and Barnett* [1970], since the lattice parameter determinations show less scatter and the measurements were made over a pressure range nearly three times as large as that of *Bassett and Barnett* [1970].

Measurements of linear compressibilities on materials isostructural with stishovite have been made by various techniques. *Bridgman* [1928], using the techniques of dilatometry, measured the linear compressibilities for rutile. The pressure dependence of the axial ratio based on his measurements can be expressed as

$$\Delta c/c_0 = 0.553\ \Delta a/a_0$$

On the basis of the ultrasonic techniques, *Verma* [1960] (recalculated by *Birch* [1960]) determined the linear compressibilities along the *c* and *a* axes for rutile. The pressure dependence of the axial ratio can be expressed as

$$\Delta c/c_0 = 0.451\ \Delta a/a_0$$

Manghnani [1969] also determined the elastic parameters of a single-crystal rutile by ultrasonic measurements and calculated the ratio of the axial compressibilities as

$$\Delta c/c_0 = 0.449\ \Delta a/a_0$$

The pressure dependence of the axial ratio for the rutile structure of GeO_2 was recently calculated from measuring elastic constants of a single-crystal sample by *Wang and Simmons* [1973] by means of ultrasonic techniques. Their results can be expressed as

$$\Delta c/c_0 = 0.369\ \Delta a/a_0$$

Clendenen and Drickamer [1966], using high-pressure X ray techniques, measured the effect of pressure on the lattice parameters of three rutile structure minerals, cassiterite, pyrolusite, and rutile, by using three diffraction peaks. Since their reported linear compressibilities for rutile are in serious disagreement with those reported by Bridgman, Verma, and Manghnani, their values for rutile as well as those for cassiterite and pyrolusite are probably less reliable. Thus the ratios $(\Delta c/c_0)/(\Delta a/a_0)$ for rutile observed by *Bridgman* [1928], *Verma* [1960], and *Manghnani* [1969] and those for GeO_2 (rutile) observed by *Wang and Simmons* [1973] are similar to the ratio obtained for stishovite within the experimental uncertainties. This similarity suggests that the effect of pressure on the *c*/*a* ratios for oxides having the rutile-type structure is predominantly determined by the geometry of the structure.

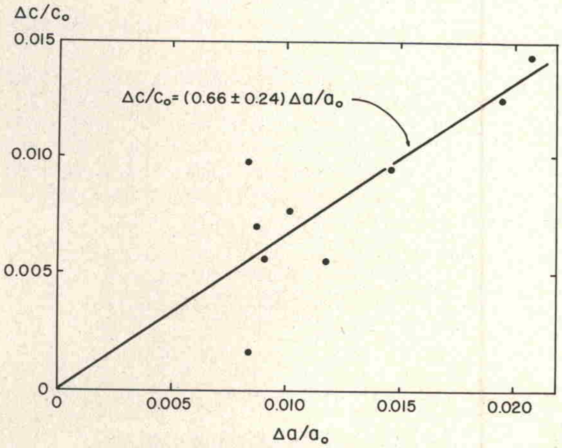

Fig. 4. Comparison between the linear compressibilities of the *a* axis and the *c* axis. The linear equation was derived by a least squares fit of all the data points.

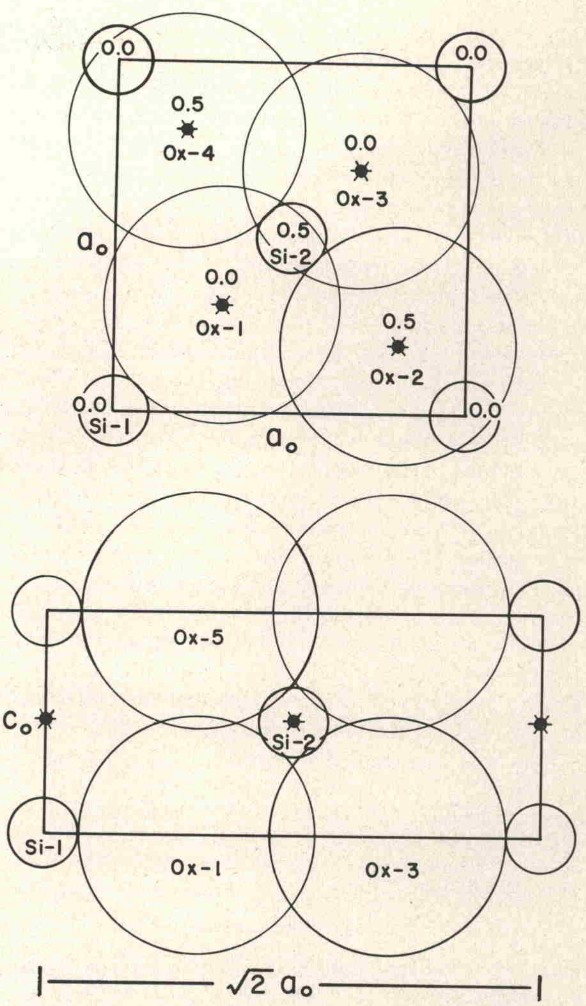

Fig. 5. The *c* axis projection and the (110) section of the stishovite structure. The upper number inside each atom gives the fractional distance of the atom along the axis perpendicular to the plane of the diagram. The O*x* and Si represent oxygen and silicon, respectively. The radii of the circles are consistent with the ionic radii, R_{ox} = 1.40 Å and R_{Si} = 0.41 Å [*Pauling*, 1960]. The value of *u* is 0.307 (J. S. Weaver, personal communication, 1970). The stars in the diagrams indicate the points at which chains of nearest-neighbor atoms pass through perpendicular to the planes of the diagrams.

The difference in linear compressibilities along the *c* axis and the *a* axis of stishovite must reflect the anisotropy of the atomic arrangement and bonding. For this reason we next examine the crystal structure of stishovite. Although no single-crystal studies of stishovite have been made, the powder diffraction data indicate that it is isostructural with rutile and therefore belongs to the space group $P4_2/mnm$. The intensities of the reflections in the powder diffraction pattern are consistent with a value of 0.307 for *u*, the positional parameter for the oxygens (J. S. Weaver, personal communication, 1970). This is close to the value of *u* for rutile (0.305). Figure 5 shows the *c* axis and the [110] axis projections of the structure. In these diagrams the sizes of the ions are based on the published values for the ionic radii of Si and O (0.41 and 1.40 Å, respectively [*Pauling*, 1960]).

In the stishovite structure it is possible to find straight lines or chains of nearest-neighbor ions. There are two types of these chains that can be found in the diagrams (Figure 5): (1) -(O*x*-1)-(O*x*-5)-etc., and (2) -(Si-1)-(O*x*-1)-(O*x*-3)-etc. There is one of the first type of chain passing through each of the oxygens in the *c* axis projection in Figure 5. Therefore there are four chains of the first type parallel to the *c* axis passing through the *c* axis projection of the unit cell. There are two chains of the second type passing through the (110) section, one through the Si-2 ion and one through the point halfway along the edge parallel to the *c* axis. The areas of the *c* axis projection (17.5 Å^2) and the (110) section (15.8 Å^2) are close. Thus for every two chains of the first type parallel to the *c* axis there is approximately one of the second type parallel to the [110] axis and one of the second type parallel to the [$1\bar{1}0$] axis.

These observations are consistent with the fact that the compressibility of stishovite is greater perpendicular to the *c* axis than it is parallel to the *c* axis.

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