Crystal structure and compressibility of zircon at high pressure

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Abstract

Unit-cell and crystal-structure parameters of zircon ($ZrSiO_4$, tetragonal $I4_1/amd$, $Z = 4$) have been determined at eight pressures from 1 bar to 48.1 kbar. Volume compressibility is $4.41 \pm 0.04 \times 10^{-4}$ kbar^{-1} (bulk modulus 2.27 ± 0.02 Mbar), and linear compressibilities are $\beta_{\parallel} = 0.95 \times 10^{-4}$ and $\beta_{\perp} = 1.6 \times 10^{-4}$ kbar^{-1}. Zircon is less compressible than any other measured compound with tetrahedrally-coordinated silicon.

Projections of tetrahedral Si–O bond distances to high pressure suggest that ^{IV}Si to ^{VI}Si transformations occur when the tetrahedral distance compresses to approximately 1.59A, on the basis of known transformation pressures, Si–O bond compressibilities, and room-pressure structures of several silicates. For silicates with room-pressure Si–O distances ranging from 1.61 to 1.655A, predicted transformations to 6-coordinated silicon structures will occur between approximately 100 and 300 kbar at 23°C. These transformation pressures are relatively insensitive to temperature ($dP/dT \leq 0.01$ kbar/°C), and ^{IV}Si to ^{VI}Si transitions are therefore predicted to occur primarily in the transition zone of high-density gradient of the earth's mantle. $ZrSiO_4$ is predicted to transform to a dense phase with octahedral silicon at approximately 170 kbar.

Introduction

Silicon-to-oxygen bonds are structural elements of many minerals throughout the earth's crust and mantle. The response of Si–O bonds to pressure, therefore, is an important parameter in characterizing the solid earth. Silicon is tetrahedrally coordinated in all known crustal silicates, but high-pressure transformations of silicates to forms with 6-coordinated silicon (stishovite, perovskite-type silicates) are well known. Liu (1978) has recently proposed that silicon might also enter 8-coordination in fluorite-like structures in the lower mantle, on the basis of high-pressure transformations of SnO_2 and TiO_2 to fluorite-related structures.

Bonds between oxygen and tetravalent cations have been characterized as rigid structural elements that change little, compared to weaker bonds, with changes in temperature or pressure. Zircon is an excellent structure to test this suggestion, for all metal cations are tetravalent. Furthermore, because of edge sharing between polyhedra, all changes in unit-cell volume must be accompanied by changes in metal-oxygen distances. The compressibility and thermal expansivity of zircon consequently should be among the lowest for oxygen-based compounds. The reported zircon volume thermal expansion is 1×10^{-5} °C^{-1}, which is significantly lower than that of most other silicates (typically $2-4 \times 10^{-5}$ °C^{-1}; Clark, 1966). The reported bulk modulus of nonmetamict zircon is approximately 2.3 Mbar (Özkan and Jamieson, 1978), which is larger than values for olivines, garnets, silicate spinels, and other close-packed silicates (Clark, 1966).

The crystal structure of zircon was described and illustrated by Robinson *et al.* (1971), who cited earlier studies. Finger (1973) presented revised values of zircon structure parameters. The volume compressibility of zircon has been measured by several authors (Madelung and Fuchs, 1921; Özkan and Jamieson, 1978; Singh and Kennedy, 1977). Of the previous workers, only Singh and Kennedy reported the axial compressibilities of this tetragonal mineral; however, their results have considerable scatter. The principal objective of our study was to determine the axial and volume compressibilities for zircon, to relate these compressions to changes in interatomic distances, and to compare these changes with those in other silicates at high pressure.

Table 1. Zircon unit-cell parameters and refinement conditions

P (kbar)	a (A)	c (A)	Vol. (A^3)	c/a	No. of independent observed reflections	Weighted R* (%)	R† (%)
Crystal No. 1							
1 atm – before P	6.6042(4)‡	5.9796(3)	260.80(3)	0.9054	505§	5.1	3.7
9.8(5)	6.5927(4)	5.9742(3)	259.66(2)	0.9062	74	2.7	2.8
28.9(5)	6.5737(4)	5.9638(5)	257.72(3)	0.9072	74	3.0	2.9
Crystal No. 2							
10.0(1.0)	6.5942(4)	5.9740(1)	259.77(2)	0.9059	‖		
17.4(5)	6.5849(3)	5.9693(1)	258.83(2)	0.9065	79	3.9	3.0
23.2(5)	6.5808(3)	5.9670(1)	258.37(2)	0.9067	79	3.2	2.4
37.1(5)	6.5650(3)	5.9583(5)	256.80(3)	0.9076	82	3.3	3.1
42.0(5) { before data	6.5592(4)	5.9553(5)	256.22(3)	0.9079	81	2.5	2.3
after data	6.5587(5)	5.9551(4)	256.17(4)	0.9080			
48.1(5)	6.5531(3)	5.9519(2)	255.59(2)	0.9124	73	2.8	2.6
1 atm – after P	6.6027(9)	5.9776(5)	260.62(5)	0.9054	‖		

*Weighted $R = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

†$R = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$.

‡Parenthesized figures represent esd's of least units cited.

§Data not averaged.

‖Unit-cell data only.

Experimental

Specimen description

Fragments of nonmetamict zircon from a colorless, gem-quality single crystal were kindly provided by G. L. Davis, Geophysical Laboratory. The specimen is from a kimberlite, Finsch Pipe, near Kimberley, South Africa, and has an age of 94 m.y., as determined by U/Pb dating (Davis, 1977). The zircon is nearly pure $ZrSiO_4$, with 1.2 weight percent HfO_2 and 26 ppm uranium.

High-pressure techniques

Two fragments, with the excellent parting characteristic of some kimberlite zircons, were used in high-pressure experiments. Crystal No. 1 was a rectangular (110) plate, $90 \times 90 \times 30$ μm, and crystal No. 2 was a triangular (100) plate 100 μm on a side and 35 μm thick. Crystals were mounted in a miniature opposed-diamond pressure cell (Merrill and Bassett, 1974), using Inconel 750X (International Nickel Company, Inc.) gaskets, and 4:1 methanol:ethanol as the hydrostatic pressure medium. Ruby crystals of approximately 10 μm maximum dimension were included in the mount, and pressures were calibrated to ±0.5 kbar using the pressure shift of the R_1 ruby fluorescence line (Piermarini et al., 1975).

Details of procedures for crystal mounting, crystal centering on the four-circle diffractometer, unit-cell determination, and data collection are described elsewhere (Hazen, 1976; Finger and King, 1978; Hazen and Finger, 1977).

Data collection and refinement

Intensity measurements were made on an automated four-circle Picker diffractometer with Nb-filtered Mo$K\alpha$ radiation, using the constant precision intensity technique described by Finger et al. (1973) and the fixed-ϕ mode of data collection at high pressure (Finger and King, 1978). All reflections in one octant of reciprocal space from 0.1 to 0.9 sin θ/λ were collected at room pressure, and all accessible reflections in one hemisphere of reciprocal space from 0.1 to 0.7 sin θ/λ were collected at high pressure. The number of independent observed reflections ($I > 2\sigma$), R values, and unit-cell parameters are listed in Table 1. Zircon is tetragonal, but unit-cell parameters were refined without constraint to detect crystal strain. Unconstrained parameters were dimensionally tetragonal within two esd at all pressures; at the highest pressure of 48 kbar, for example, $a_1 = 6.5531(3)$, $a_2 = 6.5531(17)$, $c = 5.9519(2)$, $\alpha = 89.993(8)$, $\beta = 90.005(3)$, $\gamma = 89.984(12)$.

The observed intensities were corrected for absorp-

Table 2. Zircon refined fractional coordinates and anisotropic temperature factors

Atom	Parameter	1 atm	9.8 kbar	17.4 kbar	23.2 kbar	28.9 kbar	37.1 kbar	42.0 kbar	48.1 kbar
Zr*	β_{11}	0.00171(9)†	0.0017(2)	0.0013(2)	0.0018(2)	0.0017(3)	0.0019(2)	0.0018(2)	0.0018(2)
	β_{22}	0.00161(13)	0.0023(5)	0.0023(3)	0.0020(3)	0.0012(6)	0.0020(2)	0.0027(2)	0.0021(3)
Si‡	β_{11}	0.00171(9)	0.0031(5)	0.0020(6)	0.0021(5)	0.0025(5)	0.0024(5)	0.0028(4)	0.0017(6)
	β_{33}	0.00161(13)	0.0022(12)	0.0028(8)	0.0028(7)	0.0023(15)	0.0021(6)	0.0027(5)	0.0040(7)
O§	y	0.0660(4)	0.0661(6)	0.0666(10)	0.0657(9)	0.0654(7)	0.0656(8)	0.0656(7)	0.0659(9)
	z	0.1951(4)	0.1962(8)	0.1963(9)	0.1951(8)	0.1954(9)	0.1961(7)	0.1960(6)	0.1956(8)
	β_{11}	0.0048(4)	0.0038(9)	0.0054(15)	0.0055(13)	0.0033(9)	0.0042(11)	0.0053(10)	0.0040(13)
	β_{22}	0.0022(4)	0.0043(9)	0.0040(13)	0.0038(12)	0.0029(10)	0.0040(10)	0.0040(8)	0.0021(13)
	β_{33}	0.0020(4)	0.0020(20)	0.0029(12)	0.0029(10)	0.0020(20)	0.0025(8)	0.0043(8)	0.0055(11)
	β_{23}	-0.0006(4)	0.0010(8)	-0.0011(11)	0.0014(10)	-0.0001(8)	0.0012(8)	0.0001(7)	-0.0014(11)

*Zr is at (0,3/4,1/8). $\beta_{11} = \beta_{22}$ and $\beta_{12} = \beta_{13} = \beta_{23} = 0$.

†Parenthesized figures represent esd's of least units cited.

‡Si is at (0,1/4,3/8). $\beta_{11} = \beta_{22}$ and $\beta_{12} = \beta_{13} = \beta_{23} = 0$.

§$x = 0$ and $\beta_{12} = \beta_{13} = 0$ for oxygen.

tion ($\mu_l = 44.3$ cm^{-1}), and refinement was accomplished using program RFINE (Finger and Prince, 1975)[1]. Neutral scattering factors of Cromer and Mann (1968) and coefficients for anomalous scattering of Cromer and Liberman (1970) were used for all atoms.

Zircon is tetragonal, space group $I4_1/amd$, with four ZrSiO$_4$ per unit cell. The structure has three atoms in the asymmetric unit, with Zr at (0,3/4,1/8), Si at (0,3/4,5/8), and O at (0,y,z). All refinements used a model with anisotropic temperature factors and an isotropic extinction correction. Anisotropic extinction corrections were refined for the room-pressure case but did not differ significantly from isotropic.

Results

Zircon compressibility

Regression analysis of unit-cell data in Table 1 yields equations that are linear in pressure (in kbar) from 0 to 50 kbar:

$$a\ (\text{A}) = 6.6042(5) - 0.00106(2)P$$
$$c\ (\text{A}) = 5.9797(4) - 0.00057(2)P$$
$$V\ (\text{A}^3) = 260.79(4) - 0.1079(15)P$$

For each of the three curves, second-order coefficients are approximately half their estimated standard deviations, so there is no significant departure from linearity in this pressure range. The linear compressibility of a (1.6×10^{-4} kbar^{-1}) is nearly twice that of c (0.95×10^{-4} kbar^{-1}), causing an increase in

c/a with increasing pressure. The observed volume compressibility, $4.14(6) \times 10^{-4}$ kbar^{-1}, is similar to previously-reported values (Singh and Kennedy, 1977), and is the lowest value recorded for any mineral with silicon in tetrahedral coordination.

The calculated volume compressibility, β, and bulk modulus, $K_0 = 1/\beta$, vary slightly depending on the form of equation of state used. A simple polynomial fit yields $4.14(6) \times 10^{-4}$ kbar^{-1} and 2.43(3) Mbar for β and K_0, respectively, whereas second-order Murnaghan and Birch-Murnaghan equations of state with assumed K_0' of 6.5 kbar (Özkan and Jamieson, 1978) yield $4.41(4) \times 10^{-4}$ kbar^{-1} and 2.27(2) Mbar for β and K_0. In either case, compressibility is significantly less than the 6.25–4.75×10^{-4} kbar^{-1} values for other mantle silicates (Clark, 1966).

High-pressure crystal structure

Refined structural parameters for zircon at 1 bar, and 9.8, 17.4, 23.2, 28.9, 37.1, 42.0, and 48.1 (all ±0.5) kbar are presented in Table 2, and selected interatomic distances and angles are listed in Table 3. The two variable positional parameters (oxygen y and z) do not vary within experimental error between 0 and 50 kbar. Changes in interatomic distances and angles, therefore, may be simply related to changes in the size of the unit cell. Weighted linear regression analysis of the metal–oxygen bond distances (in A) vs. pressure (in kbar) yields:

$$d(\text{Si–O}) = 1.622(1) - 0.00024(6)P$$
$$d(\text{Zr–O}) = 2.268(1) - 0.00016(4)P$$
$$d(\text{Zr'–O}) = 2.1285(9) - 0.00036(4)P$$

Bond compressibilities are 1.48(37), 0.71(18), and $1.69(18) \times 10^{-4}$ kbar^{-1} for Si–O, Zr–O, and Zr'–O,

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[1] Tabulated observed and calculated structure factors are available from the authors.

Table 3. Selected interatomic distances and angles

Parameter [Multiplicity]		1 atm	9.8 kbar	17.4 kbar	23.2 kbar	28.9 kbar	37.1 kbar	42.0 kbar	48.1 kbar
Si Tetrahedron Distances (Å) and Angles (°)									
Si-O	[4]*	1.623(2)†	1.616(4)	1.611(6)	1.620(5)	1.619(5)	1.613(5)	1.612(4)	1.611(5)
O-O‡	[2]	2.431(5)	2.424(8)	2.415(13)	2.426(11)	2.427(9)	2.421(10)	2.418(9)	2.412(11)
O-O	[4]	2.749(5)	2.739(8)	2.733(11)	2.748(9)	2.745(10)	2.734(8)	2.732(7)	2.734(9)
O-Si-O		97.0(2)	97.2(3)	97.1(4)	97.0(4)	97.1(3)	97.3(3)	97.2(3)	96.9(4)
O-Si-O		116.1(1)	115.9(2)	116.0(2)	116.1(2)	116.0(2)	115.9(3)	115.9(2)	116.1(2)
Zr Triangular Dodecahedron Distances (Å) and Angles (°)									
Zr-O	[4]	2.128(2)	2.127(4)	2.128(7)	2.119(6)	2.116(5)	2.115(5)	2.112(5)	2.112(5)
Zr-O	[4]	2.267(3)	2.269(4)	2.266(6)	2.263(5)	2.263(5)	2.264(4)	2.262(4)	2.257(5)
Mean Zr-O		2.198	2.198	2.197	2.191	2.190	2.189	2.187	2.185
O-O‡	[2]	2.431(5)	2.424(8)	2.415(13)	2.426(11)	2.427(9)	2.421(10)	2.418(9)	2.412(11)
O-O	[8]	2.840(1)	2.836(1)	2.834(2)	2.830(2)	2.828(1)	2.824(2)	2.822(2)	2.821(2)
O-O§	[4]	3.068(4)	3.068(6)	3.069(10)	3.054(8)	3.050(7)	3.050(7)	3.047(4)	3.046(8)
O-O	[4]	2.491(5)	2.501(9)	2.502(12)	2.484(10)	2.484(11)	2.491(9)	2.489(8)	2.483(10)
O-Zr-O		64.83(12)	64.6(2)	64.4(3)	64.8(3)	64.8(3)	64.7(3)	64.6(2)	64.6(3)
O-Zr-O		80.43(6)	80.3(1)	80.3(1)	80.4(1)	80.4(1)	80.25(10)	80.3(1)	80.3(1)
O-Zr-O		68.95(10)	69.2(2)	69.3(3)	69.0(2)	69.0(2)	69.2(2)	69.3(2)	69.2(2)
O-Zr-O		92.22(3)	92.29(5)	92.29(6)	92.23(5)	92.25(6)	92.30(4)	92.30(4)	92.26(5)
Cation-Cation Distances (Å)									
Zr-Zr		3.6247(2)	3.6190(2)	3.6149(9)	3.6124(5)	3.6093(2)	3.6046(7)	3.601(3)	3.5986(5)
Zr-Si		2.9898(1)	2.9870(2)	2.9845(1)	2.9834(1)	2.9819(2)	2.9790(2)	2.978(3)	2.9759(1)
Zr-Si		3.6247(2)	3.6190(2)	3.6149(9)	3.6124(5)	3.6093(2)	3.6046(7)	3.601(3)	3.5986(5)

*Bracketed figures represent bond multiplicities.
†Parenthesized figures represent *esd*'s of least units cited.
‡Edge shared between tetrahedron and dodecahedron.
§Edge shared between two dodecahedra.

respectively. Polyhedral volume compressibilities are 0.44(11) and 0.36(6) Mbar^{-1} for the silicon tetrahedron and the zirconium dodecahedron, respectively.

The anisotropies in zircon unit-cell compression are a direct consequence of the anisotropic pressure response of the zirconium polyhedron. The Zr'-O bonds that are approximately parallel to *a* compress more than twice as much as the Zr-O bonds that are nearly parallel to *c*. A major difference between Zr-O and Zr'-O bonds is that the oxygen atoms in Zr-O bonds form shared edges, whereas those in Zr'-O bonds are primarily corner-shared. The relative incompressibility of Zr-O bonds compared to Zr'-O bonds may thus be due to a combination of symmetry restraints and to R^{4+}-R^{4+} repulsion across the shared edge.

Thermal ellipsoids

Orientations and magnitudes of zircon thermal ellipsoids are presented in Table 4 for eight pressures. Thermal ellipsoids are sensitive to errors in absorption corrections, both from the zircon crystal and from the diamond cell. It is significant, therefore, that no variations are observed within experimental error for any thermal parameter between 0 and 50 kbar, in spite of the fact that the 1 bar data were collected in air, the 9.8 and 28.9 kbar data were collected on crystal No. 1 in one diamond cell, and the other high-

pressure data were collected on crystal No. 2 in a different diamond cell.

Discussion

Bulk moduli of R^{4+} polyhedra

Compression data are now available for three types of R^{4+} polyhedra: $^{IV}Si^{4+}$, $^{VI}Si^{4+}$, and $^{VIII}Zr^{4+}$. Bulk moduli of silicon tetrahedra in olivines, spinels, garnets, pyroxenes, phlogopite, gillespite, and zircon are consistent with a value of 2.5(4) Mbar. The zirconium dodecahedron of this study has a bulk modulus of 2.8(3) Mbar. Stishovite, SiO_2 with silicon in octahedral coordination, has a bulk modulus of 3.0 Mbar (Sato, 1977), which is also the bulk modulus of the silicon polyhedron (stishovite is an example of a constrained structure in which volume compression is directly related to polyhedral compression; Finger *et al.*, 1977). Thus the simple relationship of increasing compressibility with increasing size found by Hazen and Prewitt (1977) does not appear to apply to polyhedra with tetravalent cations. For example, silicon tetrahedra, although the smallest of the three R^{4+} polyhedra examined, are the most compressible. The $^{VI}Si^{4+}$-O bond, with a Pauling bond strength of 4/6, is *more* rigid than the $^{IV}Si^{4+}$-O bond, with bond strength 4/4. This behavior may in part be due to oxygen-oxygen repulsion, for the mean O-O bond

Table 4. Orientation and magnitudes of zircon thermal ellipsoids*

Atom	Parameter	1 atm	9.8 kbar	17.4 kbar	23.2 kbar	28.9 kbar	37.1 kbar	42.0 kbar	48.1 kbar
Zr	$r_\parallel$	0.054(2)†	0.065(7)	0.054(2)	0.060(4)	0.047(11)	0.060(3)	0.063(3)	0.061(4)
	$r_\perp$	0.062(1)	0.062(2)	0.064(4)	0.063(4)	0.061(5)	0.064(1)	0.069(3)	0.063(4)
	$B_{eq.}$	0.28(1)	0.31(4)	0.27(3)	0.30(3)	0.25(4)	0.31(3)	0.33(2)	0.31(3)
Si	$r_\parallel$	0.058(5)	0.063(18)	0.071(10)	0.071(9)	0.064(2)	0.061(9)	0.070(7)	0.062(3)
	$r_\perp$	0.065(3)	0.083(5)	0.067(9)	0.068(8)	0.074(8)	0.072(7)	0.078(7)	0.085(7)
	$B_{eq.}$	0.31(2)	0.47(6)	0.37(7)	0.38(6)	0.39(7)	0.37(5)	0.45(4)	0.39(6)
O	$r_\parallel$	0.103(5)	0.092(11)	0.099(14)	0.110(13)	0.085(12)	0.096(13)	0.093(10)	0.093(19)
	$r_{\perp}1$	0.054(8)	0.055(31)	0.065(19)	0.060(18)	0.060(29)	0.059(15)	0.087(8)	0.059(14)
	$r_{\perp}2$	0.075(6)	0.101(10)	0.109(15)	0.100(12)	0.079(14)	0.098(11)	0.108(10)	0.106(10)
	α	33(14)	−17(15)	26(21)	−30(16)	5(36)	24(15)	7(81)	23(13)
	$B_{eq.}$	0.50(3)	0.57(8)	0.68(11)	0.68(10)	0.45(9)	0.59(8)	0.73(7)	0.61(10)

*For Zr and Si, one ellipsoid axis is parallel to c. For O, one axis is parallel to a, and α is the angle between the c axis and the shortest principal axis perpendicular to a.
†Parenthesized figures represent *esd*'s of least units cited.

distance in stishovite is only 2.4A, as opposed to 2.65A in silicon tetrahedra. Oxygen–oxygen repulsion does not explain, however, why the large zirconium dodecahedron with bond strength 4/8 (O–O mean distance = 2.8A) is less compressible than the silicon tetrahedron. It is possible that R^{4+}–O bonds vary considerably in degree of covalency. If Si–O bonds in tetrahedra are more covalent than octahedral Si–O or dodecahedral Zr–O bonds, then the potential minimum separation will be less well defined and might permit greater compression of the shorter ^{IV}Si–O bond.

All metal–oxygen polyhedra with +1, +2, or +3 cations previously studied have polyhedral bulk moduli significantly less than the three +4 cations described above. It is possible, therefore, to predict qualitatively the pressure response of oxygen-based compounds with both R^{4+} and lower valence cations. There is, however, no procedure now available for predicting the relative values of the small but real compressibilities of different R^{4+} polyhedra.

Tetrahedral-to-octahedral silicon transitions

Recent high-pressure experiments have demonstrated that silicon will enter 6-coordination in some mantle phases (Ringwood, 1975). Coesite (SiO_2; Si–O = 1.61A), for example, transforms to stishovite at 80 kbar (Yagi and Akimoto, 1976). All silicates measured are observed to have similar mean tetrahedral Si–O compressibilities of $1.3(2) \times 10^{-4}$ kbar^{-1}, so the predicted mean Si–O distance in coesite at the 80 kbar transition is approximately 1.59A. Enstatite ($MgSiO_3$; Si–O = 1.63A) transforms to an ilmenite-

type structure at about 250 kbar (Liu, 1976; Ito, 1977). The predicted Si–O distance for enstatite at this transformation is again approximately 1.59A. Olivine [$(Mg,Fe)_2SiO_4$; Si–O = 1.65A] transforms to a silicate spinel at pressures between 50 and 100 kbar. At room pressure the silicate spinel Si–O bond distance is 1.655, and the Si–O compressibility is approximately 1.2×10^{-4} kbar^{-1} (Finger, Hazen and Yagi, in preparation). This phase transforms to a perovskite structure at approximately 270 kbar (Liu, 1976), at which pressure the spinel Si–O distance is projected to be 1.60A. Orthoclase and albite (Si–O = 1.61A in ordered tetrahedra) transform to dense assemblages with octahedral silicon at approximately 100 kbar (Ringwood, 1975), and the projected Si–O distance is once again 1.59A. It appears, therefore, that for silicate transformations from 4-coordinated to 6-coordinated silicon, the Si–O distance of the phase with tetrahedral silicon does not compress below 1.59A.

The longest recorded mean Si–O tetrahedral bond distance is approximately 1.655A in silicate spinels (Finger *et al.*, 1977), whereas the shortest Si–O bonds are approximately 1.61A in framework silicates. If 1.59A represents a minimum Si–O distance, then the range of pressures at which transformations from 4- to 6-coordinated silicon may occur is from about 100 kbar (for framework silicates) to about 300 kbar (for orthosilicates). Temperature is observed to have relatively little effect on the pressures of 4-to-6 transformations (for coesite to stishovite the temperature effect is 0.01 kbar/°C; Yagi and Akimoto, 1976). The range of 4-to-6 transformations, therefore, corresponds to a depth in the earth of approximately 300

to 900 km, which is the transition region of rapidly increasing density with depth.

High-pressure transformations of zircon

The minimum Si–O distance may also be used to predict high-pressure transformation conditions for $ZrSiO_4$. Zircon is known to transform to the scheelite ($CaWO_4$) structure at approximately 120 kbar (Reid and Ringwood, 1969); these two structures are closely related, however, varying only slightly in the arrangement of silicon and zircon polyhedra, and it is plausible to assume that the 1 bar Si–O distances and compressibility are similar for the scheelite-like and zircon polymorphs. The Si–O bond should compress to 1.59Å at approximately 160 kbar. For higher pressures the scheelite-like phase will probably transform to a phase with 6-coordinated Si. Ringwood (1975) has suggested the $KAlF_4$ structure type as the post-scheelite form of $ZrSiO_4$. If a bulk modulus of 3 Mbar is assumed for octahedrally-coordinated silicon, the ^{VI}Si–O distance would compress from the 1 atm value of approximately 1.78Å (Baur and Khan, 1971) to 1.74Å at the proposed transition pressure of 160 kbar. If the Si–O polyhedron is regular, as observed for $KAlF_4$ (Brosset, 1938), the resulting cell would correspond to a volume reduction of 30 percent at the 160 kbar transition. Furthermore, the Zr–O polyhedron would be a cube with a Zr–O distance of 2.8Å. It appears, therefore, from predicted bond distances and unit-cell volume, that the $KAlF_4$ structure is quite reasonable for the post-scheelite phase of $ZrSiO_4$.

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