Crystal Chemistry of Silicon–Oxygen Bonds at High Pressure: Implications for the Earth's Mantle Mineralogy

Abstract. *Transformations involving a change from tetrahedrally coordinated to octahedrally coordinated silicon* ($^{IV}Si \rightarrow {}^{VI}Si$) *are observed to occur at high pressure when the mean* $^{IV}Si–O$ *bond compresses to approximately 1.59 angstroms based on known room-pressure crystal structures, Si–O bond compressibilities, and pressures of* $^{IV}Si \rightarrow {}^{VI}Si$ *transformations. The lower two-thirds of the mantle transition zone of high-density gradient (500 to 900 kilometers) corresponds to the predicted range of* $^{IV}Si \rightarrow {}^{VI}Si$ *transformations. The 10 percent density increase of this zone at zero pressure is attributed primarily to the density increase associated with the change in silicon coordination. Below 900 kilometers all silicon is predicted to be in octahedral or greater coordination. The concept of cation polyhedral stability fields is defined.*

Silicon is one of the most abundant cations in the earth's mantle and is a major element in most proposed mantle minerals. The high-pressure crystal chemistry of Si^{4+}, consequently, is important in modeling the solid earth. In all silicates formed under crustal conditions, silicon is coordinated to four oxygens (^{IV}Si), but high-pressure transformations to phases with octahedrally coordinated silicon (^{VI}Si) are well known (Table 1). Recent experiments by Liu (*1*) suggest that silicon may enter eight coordination at even higher pressures. An understanding of these high-pressure silicate transformations is essential in characterizing the earth's mantle.

Pioneering studies by Ringwood and his co-workers (*2*) have demonstrated a variety of phase transformations in mantle silicates. These transitions may be divided into two groups: (i) those involving no change of cation coordination polyhedra but a change in packing of these polyhedra (for example, olivine- to spinel-type Mg_2SiO_4, zircon- to scheelite-type $ZrSiO_4$) and (ii) those in which at least one cation coordination is increased at high pressure (for example, the ^{IV}Si-to-^{VI}Si transformations listed in Table 1). Transformations of the first type generally involve density increases of no more than about 10 percent, but the second type of transition may result in a much greater reduction of volume.

Of all common cation polyhedral units found in mantle minerals, tetrahedrally coordinated silicon has the lowest average coordination and the highest valence. To a first approximation, electrostatic charge balance as defined by Pauling's second rule (*3*) is required of the atomic topology. Any oxygen bonded to ^{IV}Si has half its total formal charge (−2) satisfied, thus precluding the close approach of many more cations. In general, oxygen anions in SiO_4^{4-} groups are coordinated to no more than three additional cations. For example, each oxygen is coordinated to only two Si cations in quartz and to one Si and three $^{VI}Mg^{2+}$ or $^{VI}Fe^{2+}$ in olivine or silicate spinels (*4*). This low coordination of oxygens by cations leads to inefficient packing of cation polyhedra. In olivine and silicate spinel, even though the oxygens are approximately closest packed, only one-half of the potential octahedral sites and only one-eighth of the potential tetrahedral sites are occupied. The density of silicates with silicon in tetrahedral coordination, therefore, appears to be severely restricted by the inefficiency of packing SiO_4^{4-} units.

Another severe restriction on packing of silica tetrahedra is that tetrahedral faces are unlikely to be shared with faces

Table 1. High-pressure $^{IV}Si \rightarrow {}^{VI}Si$ transformations.

Formula	^{IV}Si phase	^{VI}Si phases	Transition pressure, P_T (kbar)	Density increase* (%)	$\bar{\beta}_{Si-O}$† ($Mbar^{-1}$)	d_0(Si–O) (Å)	d_{P_T}(Si–O)‡ (Å)	Reference
SiO_2	Coesite	Stishovite	80 ± 2	50	0.13	1.610	1.59	(*7*)
Al_2SiO_5	Kyanite	Corundum + stishovite	160 ± 20	11	0.13	1.630	1.595	(*9*)
$MgSiO_3$	Clinoenstatite → [stishovite + β-Mg_2SiO_4] →	Ilmenite-type	[170] → 250	[10] → 10	[0.13] → 0.15	[1.630] → 1.655	[1.59] → 1.59	(*10, 11*)
$FeSiO_3$	Clinoferrosilite → [stishovite + γ-Fe_2SiO_4] →	Wüstite + stishovite	[150] → 250	[10] → 10	[0.13] → 0.15	[1.630] → 1.655	[1.59] → 1.59	(*12*)
$CaSiO_3$	Wollastonite	Perovskite-type	160		0.13	1.630	1.595	(*13*)
$ZnSiO_3$	Zinc pyroxene	Ilmenite-type	180		0.13	1.630	1.59	(*11*)
Mg_2SiO_4	Magnesium silicate spinel	Perovskite-type + periclase	270	~10	0.15	1.655	1.59	(*10*)
Fe_2SiO_4	Ferrous silicate spinel	Wüstite + stishovite	~250	~10	0.15	1.655	1.59	(*12*)
Ni_2SiO_4	Nickel silicate spinel	NiO + stishovite	190		0.15	1.655	1.61	(*14*)
Co_2SiO_4	Cobalt silicate spinel	CoO + stishovite	180 ± 10		0.15	1.655	1.61	(*15*)
$NaAlSi_2O_6$	Jadeite	$NaAlSiO_4$ (calcium ferrite-type)+ stishovite	180	19	0.13	1.625	1.59	(*16*)
$KAlSi_3O_8$	Orthoclase → [kyanite + coesite + $K_2Si_4O_9$ (wadeite-type)] →	Hollandite-type	[~60] → 100	[25] → 25	[0.13] → 0.13	[1.610] → 1.610	[1.595] → 1.59	(*17*)
$Mg_3Al_2Si_3O_{12}$	Pyrope	Ilmenite-type	245 ± 5	7	0.11	1.635	1.59	(*18*)

*Density increases at 1 atm, 23°C. †$\bar{\beta}_{Si-O} = [d_0(Si–O) - d_{P_T}(Si–O)]/[d_0(Si–O) \times P\ (Mbar)]$. This is the mean linear Si–O compressibility as determined from high-pressure x-ray studies; d_{P_T}(Si–O) is the Si–O distance under transition conditions and d_0(Si–O) is the distance under room conditions. ‡The Si–O distance at P_T is predicted by $d_{P_T}(Si–O) = d_0(Si–O)[1 - \bar{\beta}_{Si-O} \times P_T]$. §Bracketed quantities refer to transformation from ^{IV}Si to mixed $^{IV}Si + {}^{VI}Si$ assemblages. Calculations for both $^{IV}Si \rightarrow {}^{IV+VI}Si$ and $^{IV+VI}Si \rightarrow {}^{VI}Si$ are presented.

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of divalent or trivalent cation polyhedra. This restriction is a consequence of cation-cation repulsion, as described by Pauling's third rule (*3*). Only corner sharing and edge sharing are energetically favorable.

Packing restrictions are significantly reduced if silicon enters octahedral coordination. Oxygens in SiO_6^{8-} groups have only one-third of their formal charge satisfied; a greater number of cations, therefore, coordinate each oxygen. In stishovite (SiO_2) each oxygen is coordinated to three ^{VI}Si, as opposed to two ^{IV}Si in lower-pressure silica minerals. Similarly, in cubic perovskite-like forms of Mg-Fe-Ca silicates, each oxygen is surrounded by six cations, including two $^{VI}Si^{4+}$ and four $^{XII}R^{2+}$. The packing efficiency of cations about oxygens is thus greatly enhanced with silicon in octahedral coordination. Furthermore, face sharing between ^{VI}Si and divalent cation polyhedra is possible, as demonstrated by perovskite-type silicates.

The great increase in packing efficiency resulting from $^{IV}\mathrm{Si} \rightarrow {}^{VI}\mathrm{Si}$ phase transformations leads to the large density increases recorded in Table 1. It is expected that these transformations will represent some of the greatest density increases for mantle silicate transitions, because no other change in common cation polyhedra will result in such dramatic easing of packing restrictions.

It is intriguing to speculate on the nature of $^{IV}\mathrm{Si} \rightarrow {}^{VI}\mathrm{Si}$ phase transitions. Recent high-pressure, single-crystal x-ray studies have demonstrated that the mean compressibility of metal-oxygen bonds in a cation polyhedron, to a first approximation, is independent of structure type and is primarily a function of cation type and coordination. Silica tetrahedra, for example, have a mean linear (that is, Si–O) compressibility of 0.13 Mbar^{-1} (total variation, ± 0.02) in garnets, olivine, silicate spinels, pyroxenes, quartz, phlogopite, and other silicates (*5*). Other cations have similar constant polyhedral compressibilities. It is possible, therefore, to extrapolate structural characteristics of mantle silicates from their known room-pressure structures to their high-pressure configurations near the $^{IV}\mathrm{Si} \rightarrow {}^{VI}\mathrm{Si}$ transformations.

Calculations of mean ^{IV}Si–O distances in silicates at high pressure indicate that most of the known $^{IV}\mathrm{Si} \rightarrow {}^{VI}\mathrm{Si}$ transitions occur when the Si–O bond compresses to approximately 1.59 Å (Table 1). Framework silicates (such as quartz and feldspar) with relatively short Si–O bonds under room conditions (1.61 Å) transform to ^{VI}Si compounds at pressures near 100 kbar. Chain silicates, with Si–O bonds approximately 1.63 Å long, transform to orthosilicates with longer ^{IV}Si–O bonds or to ^{VI}Si compounds at about 180 kbar. Orthosilicates, including olivines and silicate spinels, have long Si–O bonds under room conditions (1.655 Å) and transform to ^{VI}Si forms at about 300 kbar. For each of these silicate types, the average ^{IV}Si–O bond projected to the transformation pressure is 1.59 Å, which therefore appears to be a critical value.

Additional evidence for a critical ^{IV}Si–O distance is given by Hill and Gibbs (*6*), who found an inverse correlation between the Si–O distance and the Si–O–Si angle. At angles near the limiting value of 180° a minimum Si–O distance of approximately 1.59 Å is observed. For bond lengths shorter than this critical value the repulsive energy terms may become significant and thereby limit density increases. The $^{IV}\mathrm{Si} \rightarrow {}^{VI}\mathrm{Si}$ transitions increase the Si–O separation as well as the packing efficiency. The $^{IV}\mathrm{Si} \rightarrow {}^{VI}\mathrm{Si}$ transformations occur over a limited range of pressure, from approximately 100 kbar for framework silicates to 300 kbar for orthosilicates. Below about 100 kbar all common silicates have tetrahedral silicon, and above 300 kbar all silicates are predicted to have octahedral or greater coordination of silicon.

The effect of temperature on the transition pressures of $^{IV}\mathrm{Si} \rightarrow {}^{VI}\mathrm{Si}$ structures is observed to be small; for example, for coesite → stishovite the observed pressure dependence on temperature is only 0.01 kbar per degree Celsius (*7*). The region of the earth's mantle in which $^{IV}\mathrm{Si} \rightarrow {}^{VI}\mathrm{Si}$ transitions should occur, therefore, is limited to within approximately 300 to 900 km in depth (*8*). Furthermore, the mantle is depleted in silicon relative to the crust, and chain and orthosilicates are assumed to be the common ^{IV}Si mantle minerals. This constraint further limits the region of common mineral $^{IV}\mathrm{Si} \rightarrow {}^{VI}\mathrm{Si}$ mantle transitions to approximately 500 to 900 km in depth. This range corresponds to the lower two-thirds of the mantle transition zone, which is characterized by rapidly increasing seismic velocities and density with depth (*2*). The net change in zero-pressure density between 500 and 900 km is calculated by Ringwood (*2*) to be $\approx +10$ percent, which is similar to the changes in density from pyrope, silicate spinels, and pyroxenes to ^{VI}Si assemblages. It is concluded, therefore, that the unusually high-density gradients in the lower transition zone are a direct consequence of the increased polyhedral packing efficiency resulting primarily from $^{IV}\mathrm{Si} \rightarrow {}^{VI}\mathrm{Si}$ transitions, in agreement with Ringwood's model. Furthermore, all silicates below 900 km in the earth are predicted to have silicon in octahedral or greater coordination.

Each common cation in crustal minerals has a limited number of coordination states. Furthermore, phase equilibrium studies have demonstrated that the coordination number may change during high-temperature or high-pressure transformations. It appears reasonable to conclude from these observations that each specific cation coordination group (such as $^{IV}Si^{4+}$ or $^{VI}Fe^{2+}$) has a range of pressure-temperature (*P-T*) conditions under which it may be found and other *P-T* ranges under which only higher or lower coordinations will be observed. Superposition of *P-T* polyhedral stability fields for several different cations may facilitate prediction of the structural state and stability of minerals, glasses, and liquids. Silicate spinels and olivines, $R_2^{2+}SiO_4$, for example, could occur only within the coincident *P-T* fields of ^{IV}Si and $^{VI}R^{2+}$. Delineation of these *P-T* polyhedral stability fields, as in the case of ^{IV}Si and ^{VI}Si, will enhance our ability to model processes within the earth.

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References and Notes

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