

High-Pressure Framework Silicates

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Recent syntheses of high-pressure alkali and alkaline earth silicates reveal a class of framework structures with corner-linked 4- and 6-coordinated silicon. These compounds possess the structural formula $(A_{4-2x}^{1+}B_x^{2+})Si_m^{IV}(Si_n^{IV}O_{2(m+n)+2})$, where x , m , and n specify the amounts of alkaline earth, 6-coordinated silicon, and 4-coordinated silicon, respectively. Appropriate values of m and n yield a range of high-pressure structures, from fully 4-coordinated to fully 6-coordinated silicate frameworks. Recognition of this class of framework silicates leads to predictions of high-pressure structures as well as room-pressure isomorphs of high-pressure silicates.

Framework structures, which feature corner-linked three-dimensional (3D) networks of relatively rigid structural elements, encompass a varied group of natural and synthetic compounds of importance in condensed-matter physics, crystal chemistry, the earth sciences, materials science, and industry. Most of these networks form at low pressure entirely from tetrahedral elements, such as SiO_4 , AlO_4 , or PO_4 . Examples include silica minerals, feldspars, feldspathoids, and zeolites, which are major components in most crustal rocks, cement, porcelain, and other ceramics (1). Other low-pressure framework structures, including titanium and zirconium phosphates, silicates, and vanadates, incorporate network-forming octahedra such as TiO_6 or ZrO_6 along with tetrahedra. To these compounds we add high-pressure framework silicates with alternating groups of 4- and 6-coordinated silicon.

Distinctive, often commercially valuable, crystal chemical behavior arises from 3D bonding of rigid corner-linked units into a framework with cages or channels large enough to hold alkali or alkaline earth cations. The activation energy needed to break silicon- or aluminum-oxygen network-forming bonds is relatively large. The energy required to bend cation-oxygen-cation angles between corner-linked polyhedra, on the other hand, is relatively small; many framework structures are thus able to distort into lower-symmetry forms or to exchange alkali and alkaline earth cations, while retaining their network topologies. These structures commonly undergo polyhedral tilt phase transitions with changes in pressure, temperature, or cation substitution (2). Aluminum phosphate, which displays reversible amorphization at high pressure, presents an extreme case of this behavior (3). Framework structures are also often

compositionally adaptable, with a range of cation substitutions. Furthermore, in many framework compounds such as zeolites, large cations move easily between sites or through structural channels (4).

Low-pressure tetrahedral framework compounds, which are relatively open low-density structures, have been classified on the basis of ring, layer, chain, cage, or channel topologies (5). High-pressure framework structures, synthesized at pressures >4 GPa, feature denser arrangements of framework polyhedra but with large sites that are appropriate for alkali or alkaline earth cations. Nine such compounds, six of them discovered in the past 3 years, contain alkali or alkaline earth cations in sites of 8 or greater coordination (Table 1). These large cation sites are similar to those found in room-pressure minerals, but they are defined by frameworks constructed of 6- as well as 4-coordinated silicon. Here we review the crystal chemical systematics of these high-pressure framework silicates, define relations among these and other high-pressure silicates, and predict other possible high-pressure phases that have not yet been synthesized.

Alkali and alkaline earth silicates, including those with frameworks of 4- and 6-coordinated silicon, may be systematized within the general formula $(A_{4-2x}^{1+}B_x^{2+})Si_m^{IV}(Si_n^{IV}O_{2(m+n)+2})$.

$(Si_n^{IV}O_{2(m+n)+2})$. This structural formula is normalized to a total formal charge of +4 for alkali plus alkaline earth cations. Given that constraint, the values of m and n restrict the topology of the silicate polyhedral array. Numerous topologically distinct Si^{IV} – Si^{IV} frameworks may be assembled from several silicate octahedral and tetrahedral modules. All of the known frameworks incorporate either individual SiO_6 octahedra or corner-sharing $n[SiO_5]$ chains of octahedra. These network-forming modules are cross-linked by a variety of tetrahedral modules, including individual SiO_4 tetrahedra, Si_2O_7 dimers, and larger rings and layers.

In a fully connected 3D network, all oxygen atoms are bridging, linking two framework-forming polyhedra. In a framework structure with both tetrahedral and octahedral modules, therefore, the number of exposed oxygen atoms (those not bonded to two octahedra) on octahedral modules must equal the number of exposed oxygen atoms on tetrahedral modules. Thus, for example, in the $(Na_2Ca)Si_2(Si_3O_{12})$ garnet framework, individual SiO_6 octahedra (each with six exposed oxygen atoms) must be linked to individual SiO_4 tetrahedra (each with four exposed oxygen atoms) in a 2:3 ratio. Similarly, equal numbers of SiO_6 octahedra and Si_3O_9 tetrahedral rings (both with six exposed oxygen atoms per module) form a 3D framework in the wadeite, benitoite, and barium germanate structures. More complicated combinations of several octahedral and tetrahedral modules can be imagined by matching of total numbers of exposed oxygen atoms for different network-forming modules. These crystal chemical requirements are clarified by a review of the known framework silicate and related structures, in order of increasing n/m (excluding magnesium silicates with Mg in octahedral coordination).

Structures with $n = 0$: Structures with no tetrahedrally coordinated silicon include those for which $m = 1$ (Ca_2SiO_4 in the

Table 1. Framework structures with alternating Si^{VI} and Si^{IV} groups.

Phases	Structure	m	n	ρ_{calc}	Reference
<i>Observed</i>					
$Ca_2Si_2^VI O_6$	Perovskite	2	0	4.25	(6)
$Ca_2Si_2^VI Si_2^IV O_{10}$	Titanite	2	2	3.20	(7)
$Na_2CaSi_2^VI Si_3^IV O_{12}$	Garnet	2	3	3.75	(8)
$Na_4Si_2^VI Si_4^IV O_{14}$	New	2	4	3.30	(9)
$K_4Si_2^VI Si_6^IV O_{18}$	Wadeite	2	6	3.08	(11)
$Ba_2Si_2^VI Si_6^IV O_{18}$	Benitoite	2	6	3.83	(12)
$Ba_2Si_2^VI Si_6^IV O_{18}$	Ba germanate	2	6	4.00	(13)
$Na_4Si_2^VI Si_6^IV O_{18}$	New	2	6	3.09	(14)
$Na_{1.8}Ca_{1.1}Si_5^VI Si_5^IV O_{14}$	New	1	5	3.19	(16)
<i>Predicted</i>					
$Ca_2Si_2^VI Si_5^IV O_{16}$	Ca germanate	2	5	2.95	(10)
$Ba_2Si_2^VI Si_6^IV O_{18}$	Beryl	2	6	3.85	(15)

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K_2NiF_4 layer structure), $m = 2$ ($\text{Ca}_2\text{Si}_2\text{O}_6$ in the perovskite framework structure), and $m = \infty$ (SiO_2 stishovite). Of these, only the perovskite structure with a 1:3 ratio of Si:O possesses a fully corner-linked framework (6). A smaller ratio of silicon to oxygen requires that some oxygen atoms be nonbridging; thus, Ca_2SiO_4 is a layer silicate. A larger ratio, as in stishovite, requires some edge-sharing or face-sharing between silicate octahedra.

Structures with $n/m = 1$: The presence of both 4- and 6-coordinated silicon increases the crystal chemical complexity of high-pressure silicates, and it provides opportunities for forming cation sites appropriate to large alkali and alkaline earth cations. One structure, that of titanite-type $\text{Ca}_2\text{Si}_2(\text{Si}_2\text{O}_{10})$ ($m = 2, n = 2$), is known with equal numbers of 4- and 6-coordinated silicon (7). This structure incorporates corner-sharing chains of silicate octahedra like those in perovskite and stishovite, but these chains are cross-linked by silicate tetra-

hedra. The case of $\text{Ca}_2\text{Si}(\text{SiO}_6)$ ($m = 1, n = 1$) is unknown. Such a mixed 4- and 6-coordinated framework structure must incorporate at least one nonbridging oxygen in the asymmetric unit because the 1:3 ratio of Si:O is too small for a framework with silicate tetrahedra.

Structures with $n/m = 1.5$: Garnet, though often classified as an orthosilicate (with isolated SiO_4 groups), behaves structurally like a framework of 4- and 6-coordinated polyhedra. Maximum Si content for a garnet has been achieved in high-pressure synthetic $(\text{Na}_2\text{Ca})\text{Si}_2(\text{Si}_3\text{O}_{12})$ (8).

Structures with $n/m = 2$: The structure of $\text{Na}_4\text{Si}_2(\text{Si}_4\text{O}_{14})$ (9) features alternating silicate octahedra and tetrahedral Si_2O_7 dimer groups (Fig. 1A). Each octahedron is surrounded by six dimers, while each dimer is linked to six octahedra in an alternating arrangement topologically similar to that of perovskite.

Structures with $n/m = 2.5$: No alkali or alkaline earth silicates with this ratio have

been identified, but the calcium germanate analog $\text{Ca}_2\text{Ge}_2(\text{Ge}_5\text{O}_{16})$ is known (10). This structure features single germanate octahedra, each linked to two single germanate tetrahedra and to four four-member tetrahedral rings (Fig. 1B). We suggest that a high-pressure calcium or barium silicate isomorph is likely. Note that the number of exposed oxygen atoms for an individual SiO_4 tetrahedron is four, whereas that of a Si_4O_{12} ring is eight. The total of 12 exposed oxygen atoms balances those of two individual SiO_6 octahedra.

Structures with $n/m = 3$: Frameworks with a ratio of three silicate tetrahedra to one octahedron (all of them with $m = 2$ and $n = 6$) encompass structural types with three-, six-, or nine-member tetrahedral rings. The first of these silicates to be described was the wadeite form of $\text{K}_4\text{Si}_2(\text{Si}_6\text{O}_{18})$ (11), which incorporates compact three-member tetrahedral rings (Fig. 1C). Two distinct high-pressure forms of $\text{Ba}_2\text{Si}_2(\text{Si}_6\text{O}_{18})$, in the benitoite (12) (Fig.

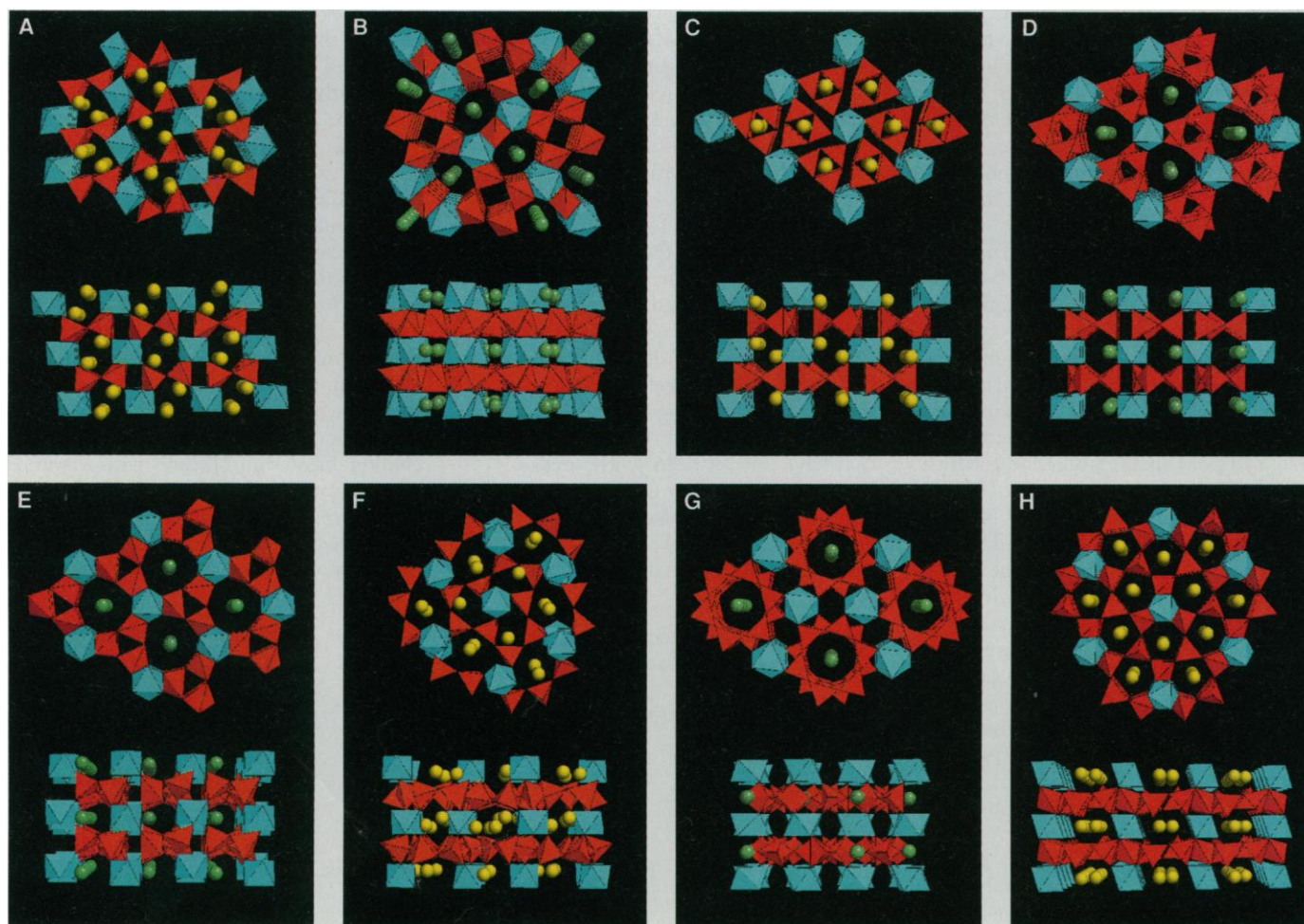


Fig. 1. Polyhedral drawings of observed and predicted framework silicates with SiO_4 tetrahedra (red), SiO_6 octahedra (blue), alkali cations (yellow spheres), and alkaline earth cations (green spheres). All structures are illustrated in views parallel and perpendicular to layers of tetrahedral groups. (A) Sodium silicate, $\text{Na}_4\text{Si}_2(\text{Si}_4\text{O}_{14})$. (B) Calcium germanate-type

$\text{Ca}_2\text{Si}_2(\text{Si}_6\text{O}_{18})$ (predicted). (C) Wadeite-type $\text{K}_4\text{Si}_2(\text{Si}_6\text{O}_{18})$. (D) Benitoite-type $\text{Ba}_2\text{Si}_2(\text{Si}_6\text{O}_{18})$. (E) Barium germanate-type $\text{Ba}_2\text{Si}_2(\text{Si}_6\text{O}_{18})$. (F) Sodium silicate, $\text{Na}_4\text{Si}_2(\text{Si}_6\text{O}_{18})$. (G) Beryl-type $\text{Ba}_2\text{Si}_2(\text{Si}_6\text{O}_{18})$ (predicted). (H) Sodium-calcium silicate, $\text{Na}_{1.8}\text{Ca}_{1.1}\text{Si}_2(\text{Si}_6\text{O}_{18})$.

1D) and barium germanate (13) (Fig. 1E) structures, also consist of alternating SiO_6 octahedra and Si_3O_9 three-member rings in slightly different layered arrangements.

The $\text{Na}_4\text{Si}_2(\text{Si}_6\text{O}_{18})$ structure, with nine-member tetrahedral rings cross-linked by individual octahedra, exemplifies the complexity possible with $\text{Si}^{\text{IV}}-\text{Si}^{\text{VI}}$ frameworks (14) (Fig. 1F). Many other framework variants with $n/m = 3$ are also possible. One example is $\text{Ba}_2\text{Si}_2(\text{Si}_6\text{O}_{18})$, a hypothetical structure with six-member rings related to the beryl topology (15) (Fig. 1G). More complex structures incorporating an integral multiple of three tetrahedra in rings (that is, combinations of three- plus six-, or four- plus five-member rings) are also possible. An intriguing structural possibility, as yet unknown in silicates, is a $\text{Si}^{\text{IV}}-\text{Si}^{\text{VI}}$ framework, with individual SiO_6 octahedra cross-linking continuous $n[\text{SiO}_3]$ tetrahedral chains. A sinusoidal tetrahedral chain might be linked to form a high-density silicate structure with the $n/m = 3$ stoichiometry.

Structures with $n/m > 3$: All $\text{Si}^{\text{IV}}-\text{Si}^{\text{VI}}$ framework structures with $n/m > 3$ must have on average fewer than two exposed tetrahedral oxygens per octahedral oxygen. Thus, some tetrahedra must be bound to three tetrahedral neighbors, for example, in amphibole-type double chains (1.5 exposed oxygen atoms per Si^{IV} or in layers (one exposed oxygen atom per Si^{IV}). Indeed, in the extreme case of $m = 0$ and $n = \infty$ (SiO_2 in the coesite structure), there are no exposed oxygen atoms per Si^{IV} .

Although many framework configurations with $n/m > 3$ might be imagined, only one such structure is known. The synthesis of $(\text{Na}_{1.8}\text{Ca}_{1.1})\text{Si}(\text{Si}_5\text{O}_{14})$, a new structure with $m = 1$ and $n = 5$, does feature a silicate tetrahedral layer, but details of this structure currently defy prediction by systematic means (16) (Fig. 1H). As expected, tetrahedra are distributed in a continuous layer cross-linked by individual SiO_6 octahedra. Those layers, with interconnected 12-member rings, are unlike any other known structure. Furthermore, 2 out of every 14 oxygen atoms are nonbridging—a feature never observed in low-pressure Si^{IV} frameworks. The possibility of $\text{Si}^{\text{IV}}-\text{Si}^{\text{VI}}$ frameworks with nonbridging oxygen atoms greatly increases the range of stoichiometries, topologies, and crystal chemical behavior that must be considered in predicting related structures.

Recognition of this class of framework silicates points to new research opportunities. These phases provide a means to investigate the high-pressure behavior of large cations. As pressure is increased, the size and shape of large sites will change, providing a tuneable probe of cation-oxygen bonding, ion exchange, and phase stability.

These studies also suggest that many related structures remain to be discovered, especially through synthesis of high-pressure phases in silicate systems containing larger cations such as Rb, Cs, Sr, and Ba. Not only do these framework structures represent possible repositories of alkali and the larger alkaline earth cations in the earth's transition zone, where mixed 4- and 6-coordinated minerals are thought to be abundant (6, 17), but some of these dense framework silicates, or their room-pressure germanate and titanate isomorphs, may also provide stable long-term storage environments for Sr^{90} , Cs^{137} , Ti^{204} , and other mobile components of radioactive waste.

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Evidence for Glacial Control of Rapid Sea Level Changes in the Early Cretaceous

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Lower Cretaceous bulk carbonate from deep sea sediments records sudden inputs of strontium resulting from the exposure of continental shelves. Strontium data from an interval spanning 7 million years in the Berriasian-Valanginian imply that global sea level fluctuated about 50 meters over time scales of 200,000 to 500,000 years, which is in agreement with the Exxon sea level curve. Oxygen isotope measurements indicate that the growth of continental ice sheets caused these rapid sea level changes. If glaciation caused all the rapid sea level changes in the Cretaceous that are indicated by the Exxon curve, then an Antarctic ice sheet may have existed despite overall climatic warmth.

Sea level curves based on sequence stratigraphy (1) imply that the sea level rose and fell 100 m or so in less than 1 million years several times during the Cretaceous. These rapid sea level changes represent a paradox, because the Cretaceous climate has typically been thought to have been too warm for extensive accumulation of continental ice, which is the only known mechanism for

driving such rapid sea level changes (2). One interpretation is that sequence stratigraphic data are recording apparent sea level changes caused by regional tectonic activity (3). However, if these sea level changes are global, either there exists some non-glacioeustatic mechanism for rapidly changing sea level or the assessment of the Cretaceous as a period of continuous climatic warmth needs reevaluation.

To test whether Cretaceous sea level changes were global, we measured Sr con-

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