Silicon

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http://web.me.com/whitby/Octahedron/Welcome.html

Reference

Octahedron1stEd.pdf–bookmark SILICON–pages 259-287

Introduction

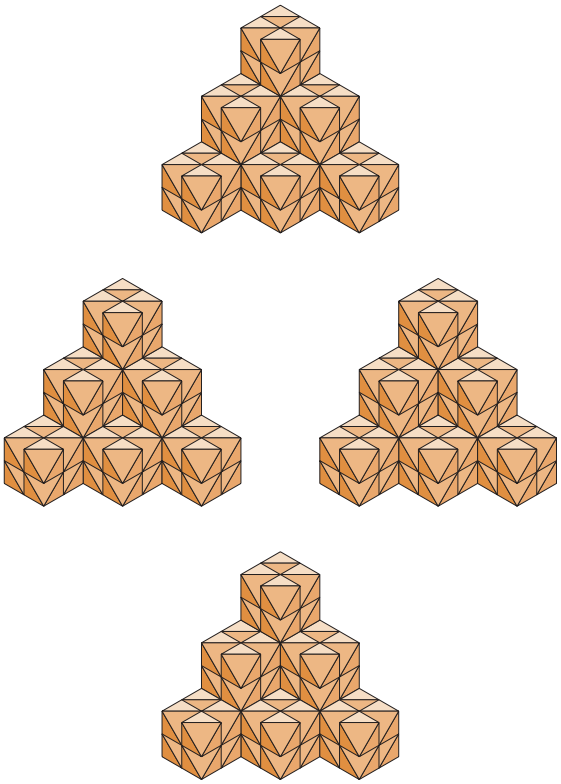
This material is excerpted from *Octahedron*. It shows how silicon atoms can join to form chains, rings, and crystals.

SILICON

Si-atom pattern is octahedral

The pattern of an image produced by Si-atoms upon a (111) surface of a Si-crystal[1] is producible using the octahedral Si-atom. The figure on the left at the bottom of the page shows a grouping of Si-atoms arranged to produce the pattern. The spacing between the Si-atoms of the ring and the two-atom groups between each pair of rings is just fillable with other Si-atoms as the figure to its right shows. The Si-atoms which have been added to the unit as spacers have a different color than the Si-atoms of the previous unit. Spacer atoms have also been included for establishing the spacing between identical units. Four units with spacers and four units without spacers are shown in the figure on the next [2]page.

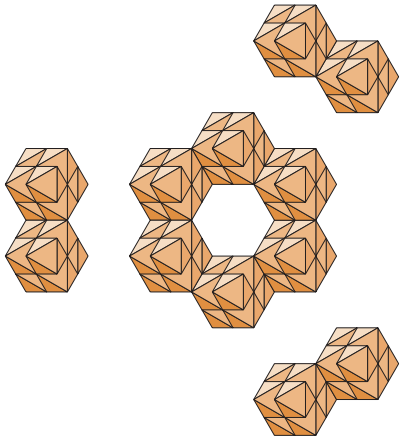
Another pattern[3] consisting of smaller bright spots isolated from one other are like the Si-octas of the Si-atoms is depicted here. The Si-octas are nearest to the viewer.

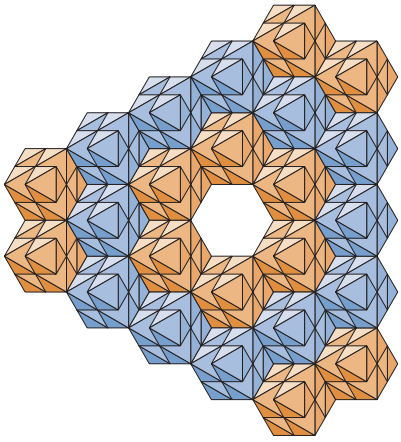


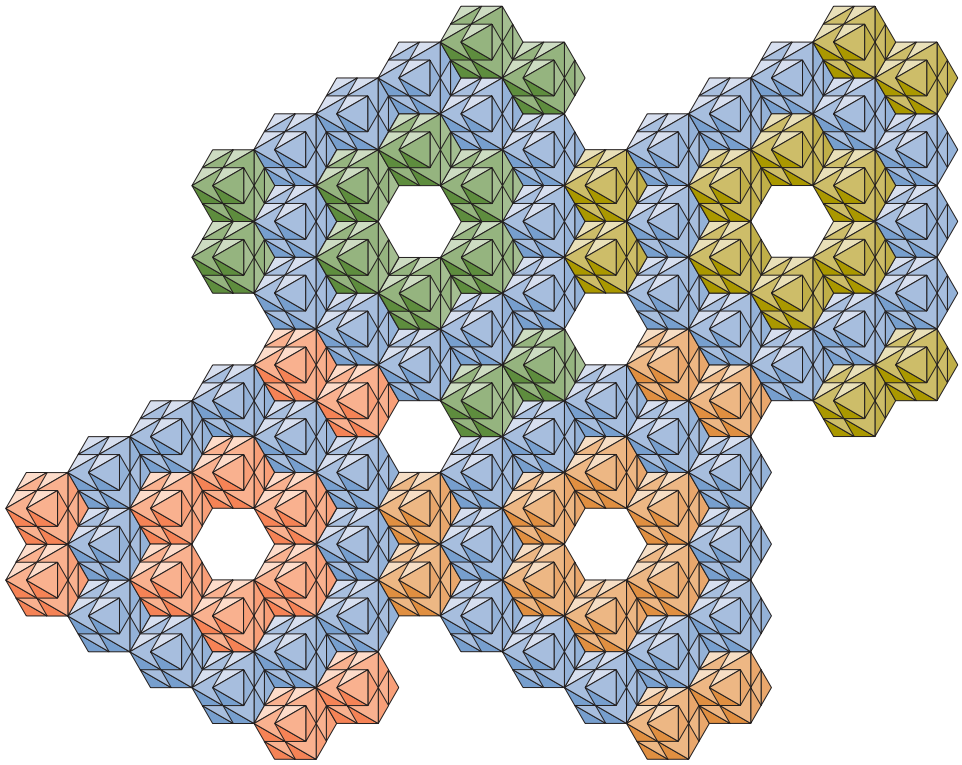
1. R. Martel, Ph. Avouris, I. -W. Lyo, Molecularly adsorbed oxygen species on Si (111)-(7x7): STM -induced dissociative attachment studies, *Science* v. 272, 19 April 1996, p. 387, Fig. 5(c). The figure is encaptioned “Empty-state STM images of a Si (111)-(7x7) surface...”

2. Hans Christian von Baeyer, *Taming of the Atom*, Random House, 1992. The same pattern is depicted here in a photograph between pages 102 and 103 which is encaptioned <Silicon atoms form a hexagonal pattern on a surface. Courtesy of IBM Research.>

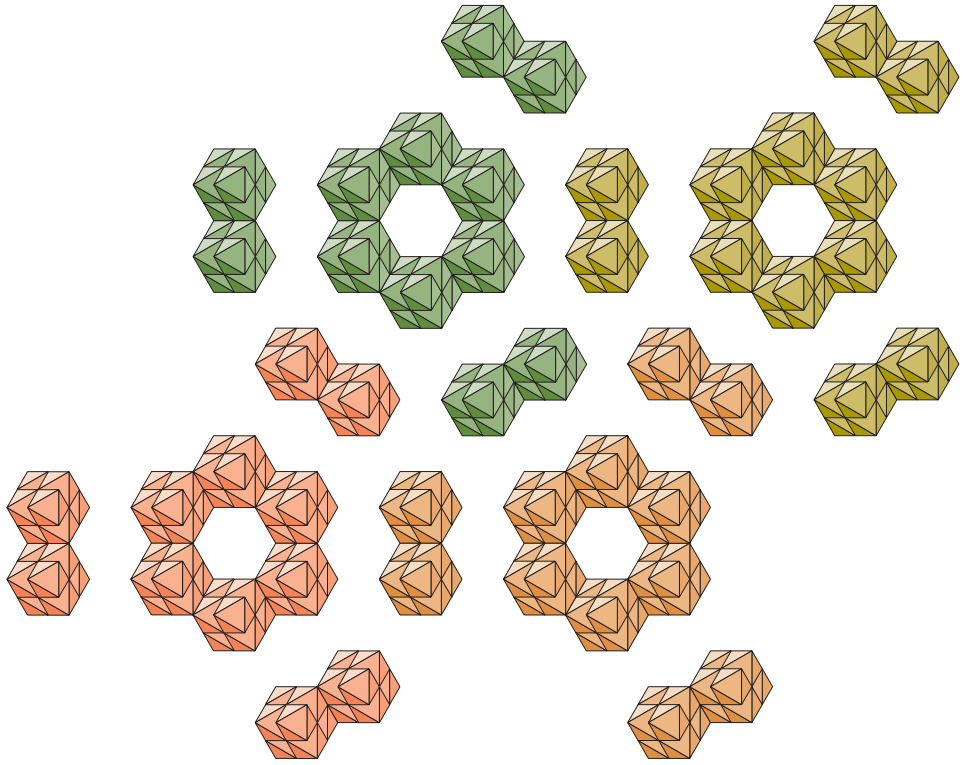
3. Baeyer, *ibidem*. A photo encaptioned <A more irregular silicon surface. Courtesy of Burleigh Instruments.>







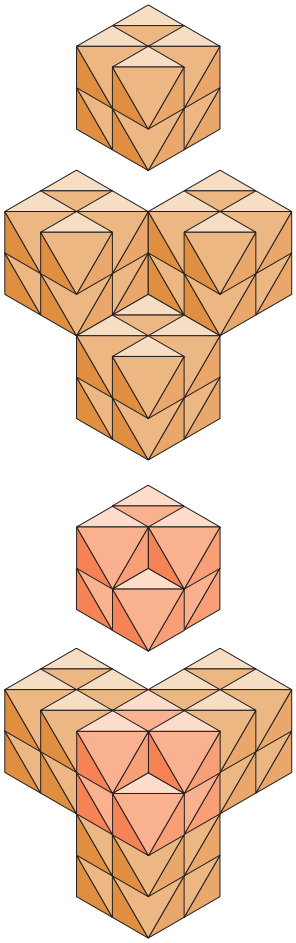
Arrangement of Si-atoms upon a Si-crystal (111) surface as shown by STM images.



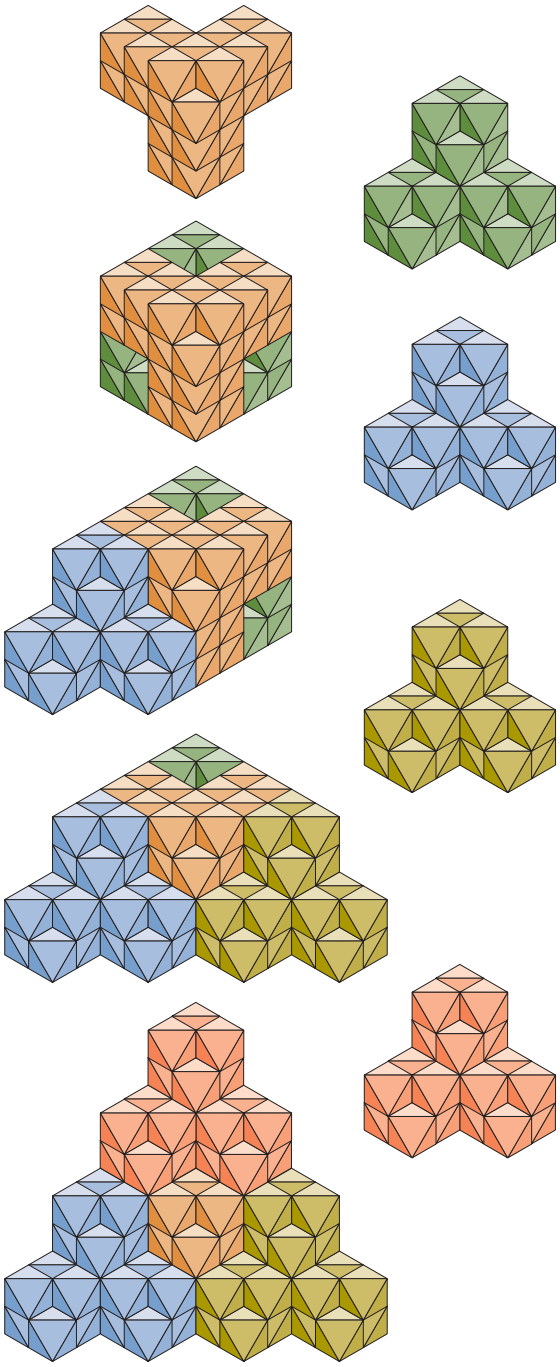
Si CFU for diamond-like cubic crystal

The crystalline structure of diamond is built of tetrahedral assemblies of four C-atoms. Four Si-atoms can join to form a regular tetrahedral assembly. These can join to form a diamond-like crystal. In the figure the assembly of a tetrahedron using four Si-atoms is shown.

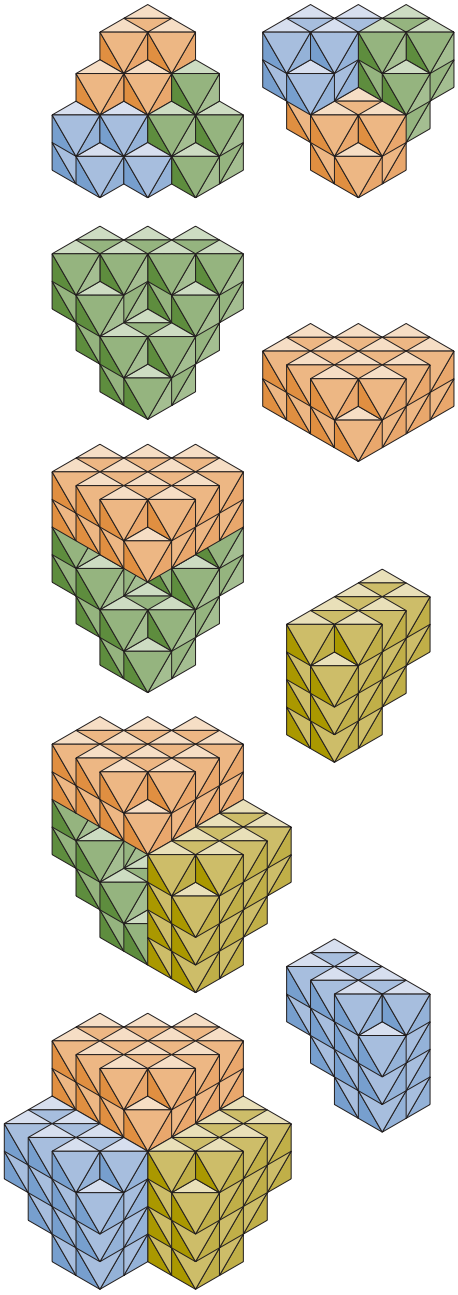
An identical tetrahedron which is inverted relative to the first tetrahedron can join facially to it.



Tetrahedral assembly of Si-atoms.
At the top, is a Si-atom with its Si-octa uppermost. Below it is a group of three identically oriented Si-atoms. Below this is a Si-atom which is inverted relative to the previous Si-atoms which completes the tetrahedral assembly shown at the bottom.



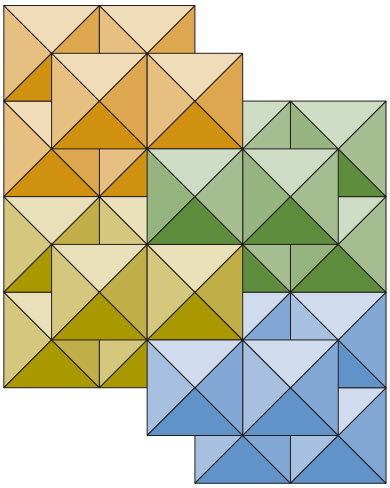
Si-atoms in diamond-like cubic crystal.
The top unit is a tetrahedral assembly of Si-atoms. In the right hand column are four identical assemblies which are inverted relative to the top unit to which they join. The units in the left column show the facial joining of the inverted units to the top unit.



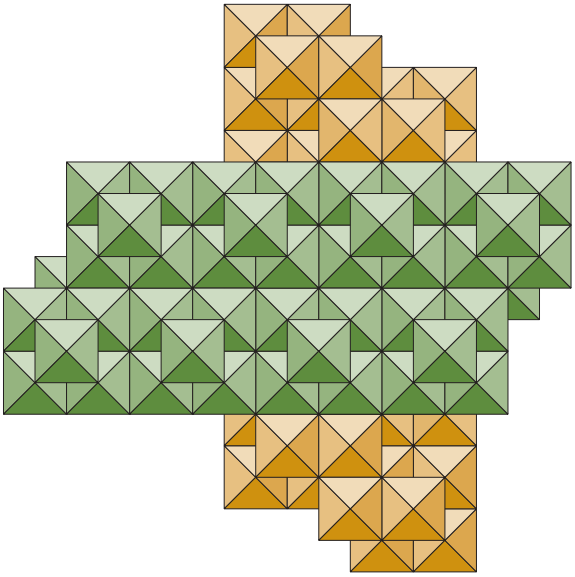
Tetrahedron formed of four panels of Si-atoms.
The top row shows two views of a panel formed by three Si-atoms. The view on the right is of the inverted panel. The panels in the right column are added to form the assemblies on the left.

Si chain

Si-atoms can be cleftly joined in a chain which is parallel to an edge of the regular octahedron. Alternate Si-atoms have the same orientation. Adjoining Si-atoms are rotated one half turn about the 16-vertexial diameter. Two of the three clefts of each Si-atom are used for the chain.



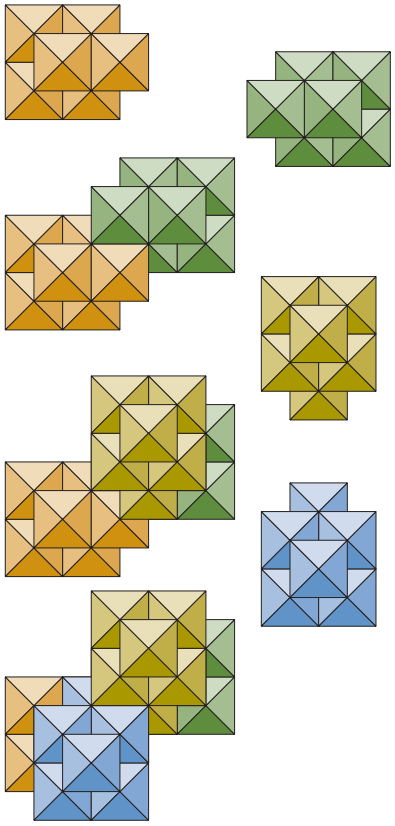
Si chain



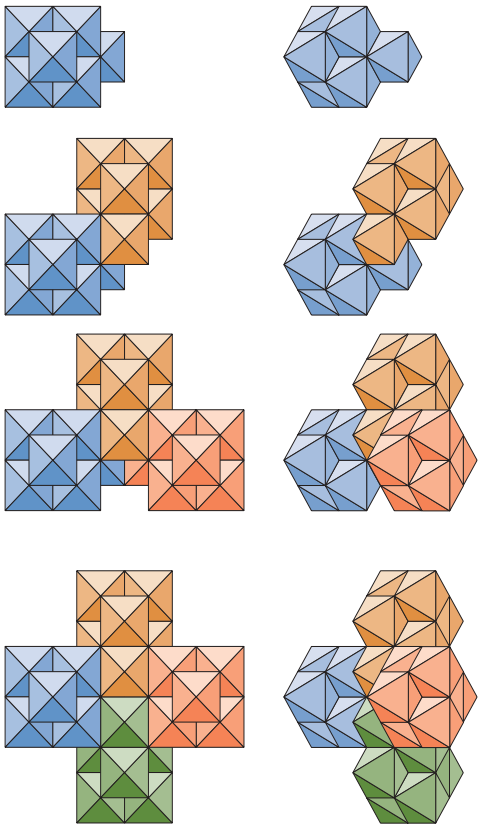
Adjoined Si chains

The third cleft is available for cleft joins with Si-atoms of an identical chain if the chain is rotated one half turn about the chain axis and crosses the first at 90°.

The parallel chains in one vertexial plane are thereby structurally included by parallel chains in an adjoining plane provided that the chains in the second plane are normal to those in the first. The outer surfaces of this paired plane of chains match up with the surface of an identical paired plane which is rotated one quarter-turn about a normal to the plane.



Joined Si of crossing chains

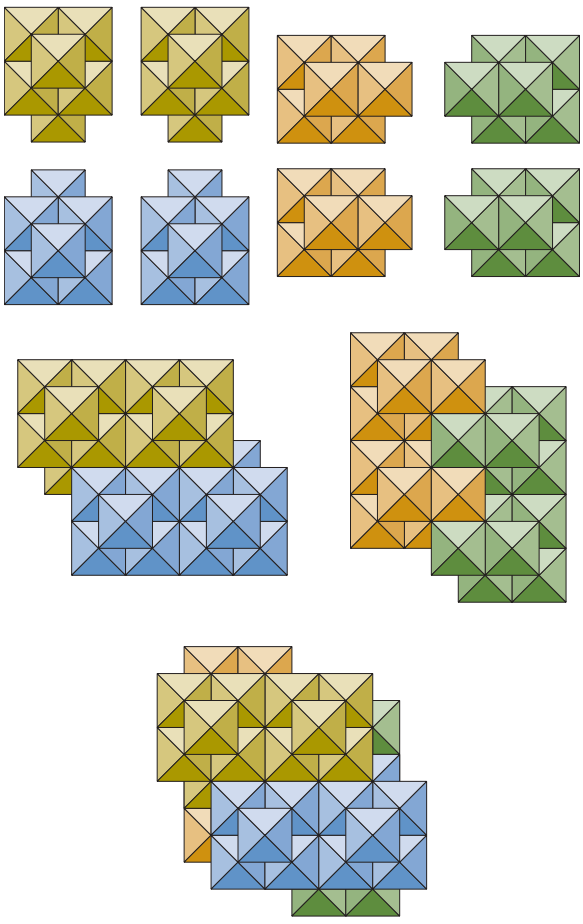


Si_4-ring assembly.

The left column shows the assembly of the Si_4-ring along the ring axis. The right column shows the assembly of the ring from another angle.

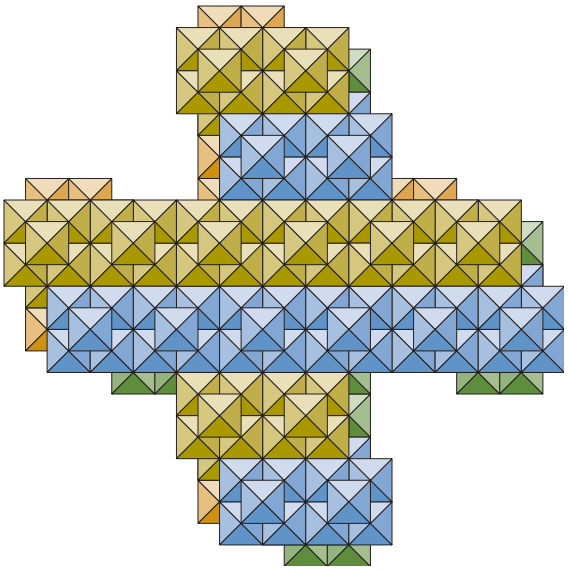
Two Si-atoms are cleftly joined to two Si-atoms of the adjoining chain. These four Si-atoms are in the form of a ring.

A paired-plane unit is formed by adding four Si-atoms to the Si chain junction. There is one Si-atom cleft for each join direction.



Paired-plane unit

In the next figure, a unit has been added to the paired-plane unit in each of the join directions.



Five paired-plane forming units

Si_4 ring

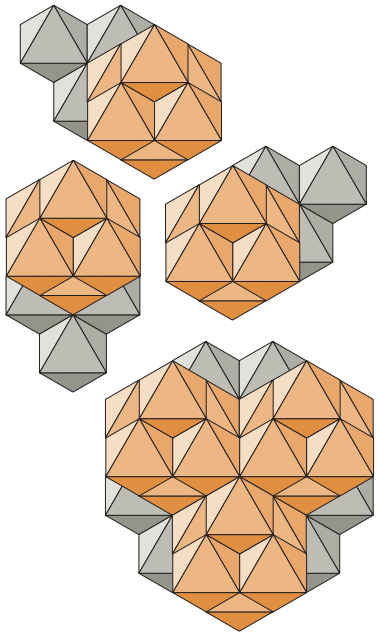
Four Si-atoms can form a ring in which each is atom is cleftly joined to two other atoms. The Si-octas of the atoms each provide a face of a regular tetrahedron.

SiC group

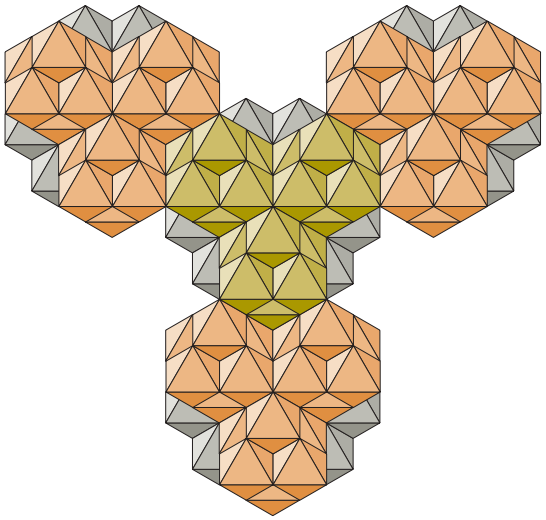
3SiC group

This is a ring of contiguous Si-atoms each of which is cleft joined to each of two C-atoms each of which is cleft joined in turn to one of the other Si-atoms. This uses two of the three clefts of each of the C-atoms and each of the Si-atoms. A cleft of each atom is left for planar join directions at 60^{o}. The units will stack normal to the plane with the 123-faces of the C-atoms bridging the gaps between the Si-atoms. This is an hexagonal arrangement. The group is a CFU. The join length in the plane is

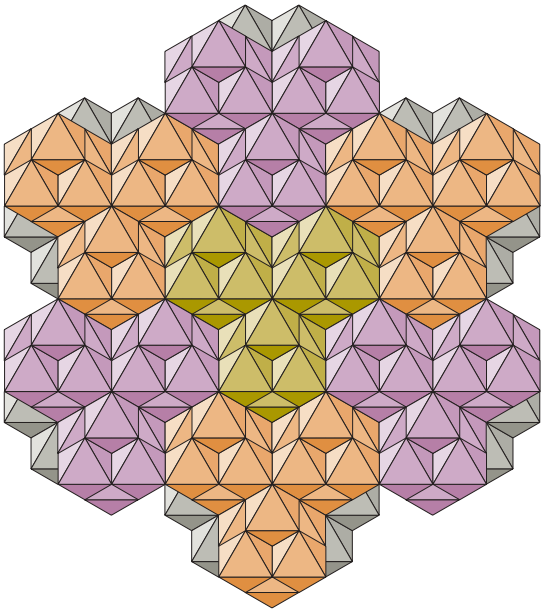
4*(sqr(3)/2)*He-octa edge and the join length for stacking is 3*sqr(2/3)*He-octa edge. This defines a volume for the cfu which is an hexagonal prism with a prism facial diameter equal to the join length in the plane and a height equal to the join length for stacking.



Formation of a SiC triplet.
Three SiC groups form a triplet in which their Si-atoms are cleftly joined by the C-atoms.

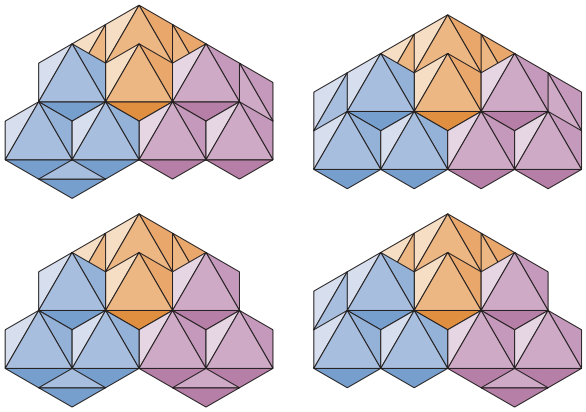


SiC triplets in planar formation
Each Si-atom of the yellow colored triplet is cleftly joined to a C-atom of each adjoining triplet.



SiC triplet with six adjoining triplets.

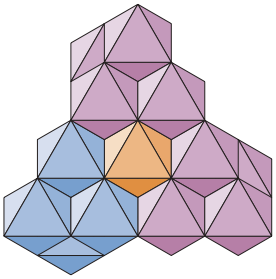
Each of the C-atoms of the central triplet is cleftly joined to the Si-atom of each of the violet colored triplets; each of the Si-atoms of the central triplet is cleftly joined to a C-atom of each of the orange colored triplets.



Three SiO_2 groups: cw, ccw, and mixed

SiO_3 group

The chemical analyses of minerals indicates that the SiO_3 group does not occur therein.



SiO_3 group

SiO_2 group

Silicon appears in the chemical analyses of rock forming minerals as SiO_2 or silica. In the next figure, there are three SiO_2 groups. They differ in the orientations of the O-atoms. In each of the two groups in the top row, the O-atoms point in the same direction, clockwise on the left and counterclockwise on the right. In the two bottom groups they point in opposite directions. There are other orientations for the O-atoms, but these are the common ring-forming orientations.

$3SiO_3$ ring not likely to exist

It is unlikely that the Si_3O_9 ring exists. Three silicon atoms can be joined so that each shares an oxygen atom with each adjoining silicon atom. A second oxygen atom attaches directly to each silicon atom but has no function in the ring formation.

The source of the SiO_4 tetrahedron fallacy

The SiO_4 seems to derive from the following. The radius ratio of the silicon ion to that of the oxygen ion indicates that 4-fold

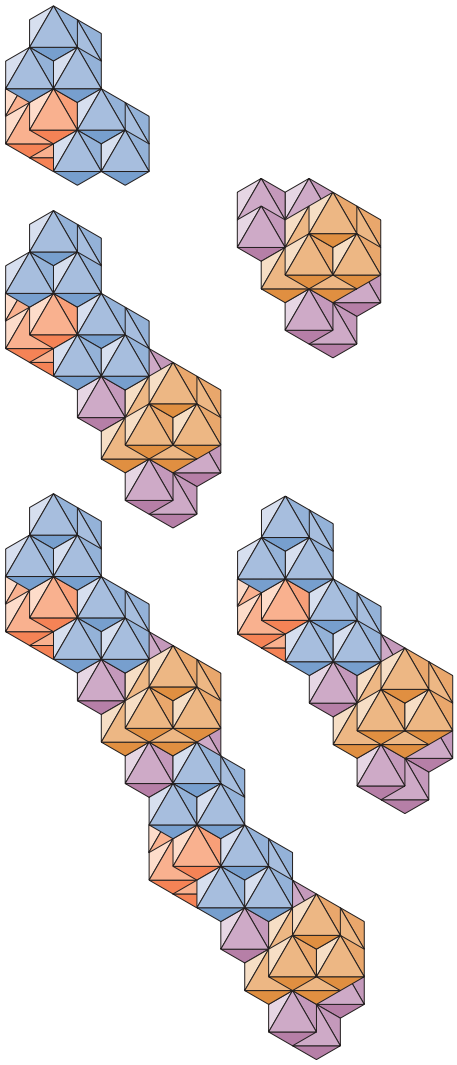
"coordination" will be the stable state of silicon-oxygen groupings. Thus, silicates are formed by a unit which has oxygen ions at the apexes of a regular tetrahedron with a silicon atom at its centroid.[1]

For the octahedral atom, this reasoning is incorrect in the following ways—

- The term ion is erroneous, there being only the atom.
- The use of radius is erroneous, the atoms not being spherical.
- The chemical analyses of crystals which are supposed to contain the tetrahedra have only SiO_2 groups.
- There are three clefts per Si-atom and these are sufficient to accommodate two O-atoms and still have the third for joining with similar units.
- Coordination derives from Lewis theory which is not applicable to the crystalline atom.

SiO_2 chain

The figure shows the assembly of a chain of identical SiO_2 groups. The two O-atoms of the group have identical orientations. Adjoining groups differ in orientation; alternate groups have the same orientation. The chain assembly begins with the joining of a pair of groups. An O-atom of one group is double cleftly joined to an O-atom of the second group. The pair is the CFU for the chain and the assembly progresses with the addition of a second pair. The chain axis is parallel to a pair of edges of the octahedra.



Silica chain

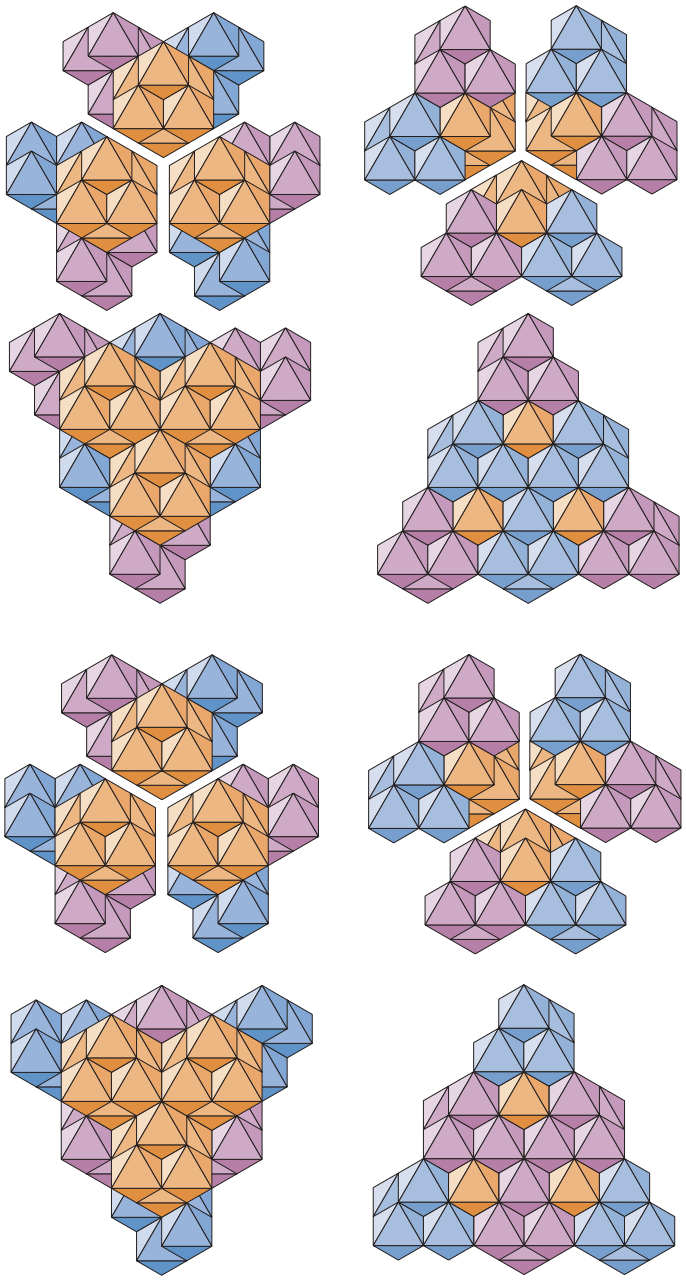
Facial SiO_2 rings

The silica group can form rings in which the axis of symmetry is parallel to a facial diameter of the octahedron.

$3SiO_2$ ring

The next figure shows rings formed by three identical silica groups.

1. C. S. Hurbut *Dana's Manual of Mineralogy* 18th ed. John Wiley 1971 p. 369

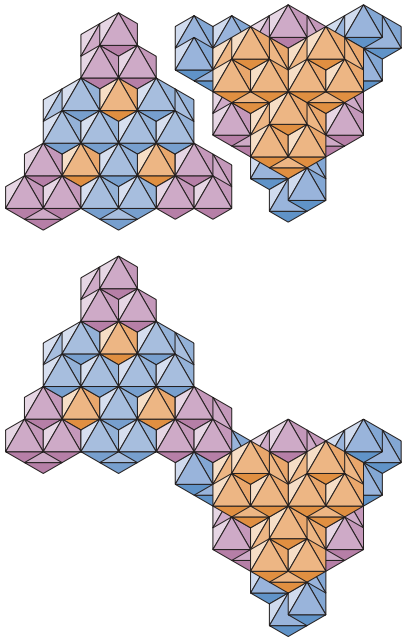


Two $3SiO_2$ rings composed of identical groups.

Two rings are produced using identical silica groups. Each of the two rings is shown in two views which differ by a rotation of one half revolution about the bottom of the page. The two views are side by side. At the top, the Si-atom of one group is cleftly joined to the blue colored O-atom of another group. At the bottom, the Si-atom of one group is joined to the violet colored O-atom. The unjoined O-atoms of the top ring have a cw-sense and those of the bottom ring have a ccw-sense in the view of each ring shown in the right hand column, where the Si-octas of the Si-atoms are uppermost.

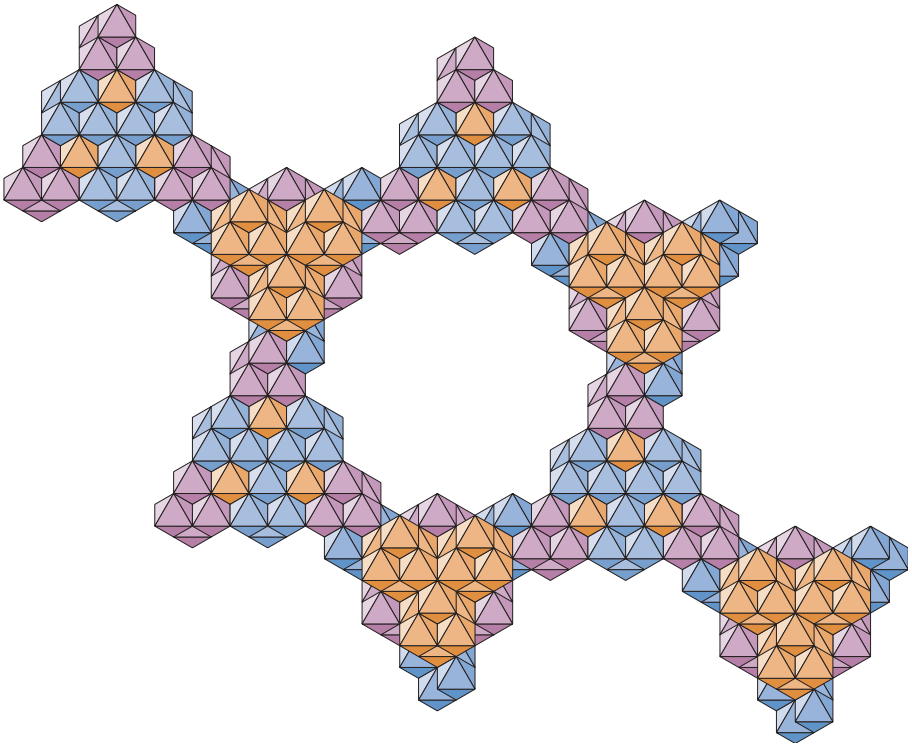
Pair of 3 SiO_2 rings, ccw & ccw

A CFU can be constructed using a 3SiO2 ring of each type. In one of the rings, the Si-octa of each Si-atom is towards the viewer; in the other ring, the Si-Octa of each Si-atom is away from the viewer. A double clefted join between an O-atom of each ring forms the CFU. This assembly is shown in the next figure.



CFU formed by the pairing of 3 SiO_2 rings, cw & ccw

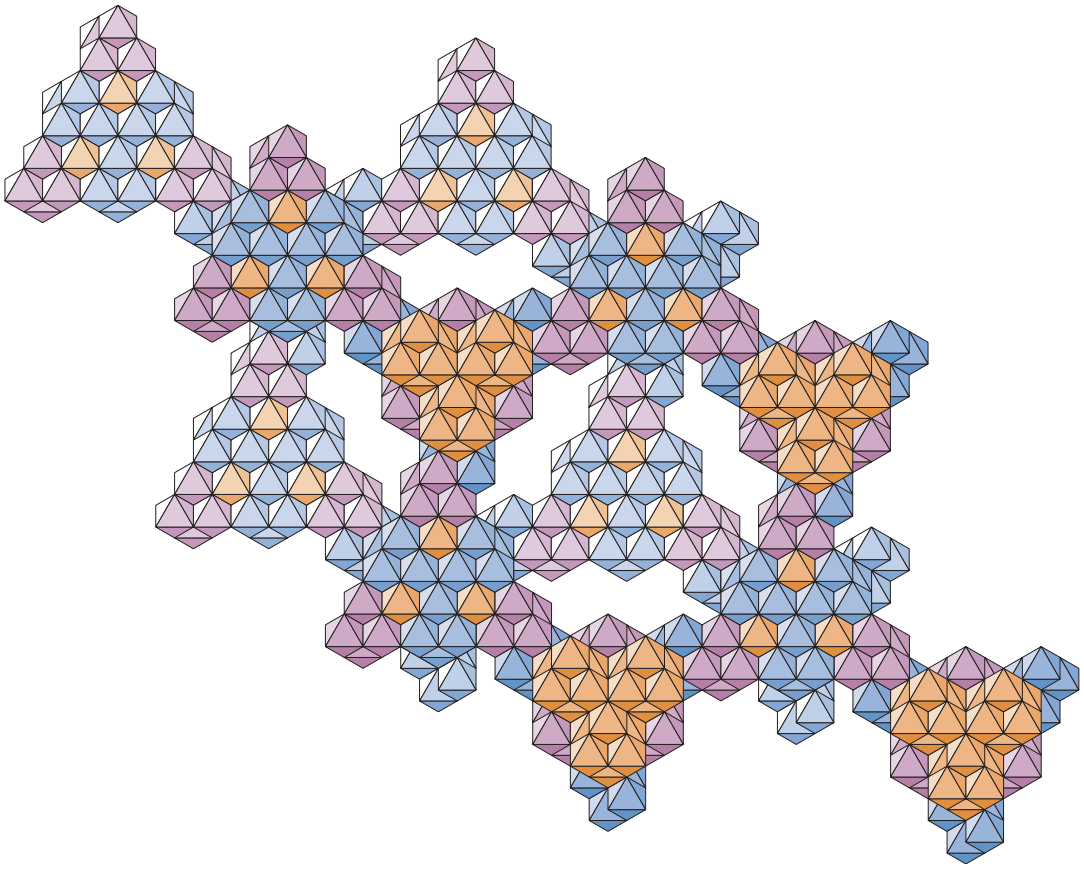
Planar assembly of 3 SiO_2 rings

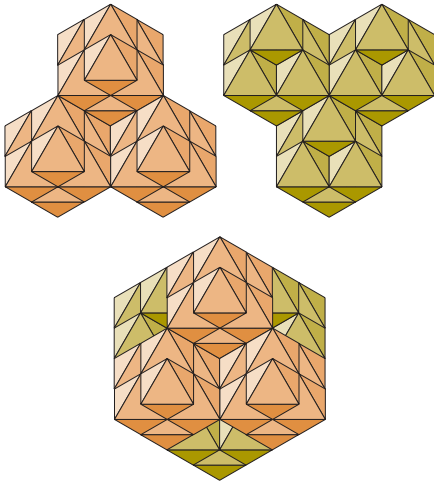


Planar assembly of four $3SiO_2$ CFUs.

O-atoms of identical CFUs are double-cleftly joined to form a planar crystal. Four CFUs are so joined in the figure and form a ring. Within the extended crystalline plane, each CFU is joined to four CFUs and each $3SiO_2$ ring is joined to three rings, one of which is the CFU of which it is a part.

Interlayer join of 3 SiO2 ring layers





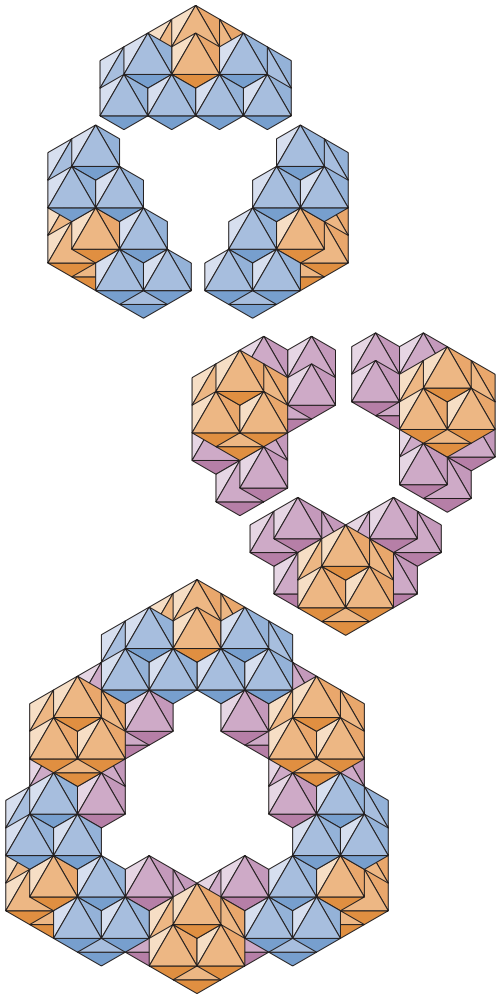
Interlayer joining of Si-atoms in $3SiO_2$ crystal

The planar crystals join through the formation of octahedral groupings which result from the pairing of the Si-atom triplet of a $3SiO_2$ ring of one plane with that of an adjoining plane. The figure to the left shows the relationship between the Si-atom triplets.

The figure above shows two planar rings of four CFUs each which are joined by the pairing of the Si-atom triplets. One of the two $3SiO_2$ rings of each CFU joins with the ring of a CFU of the planar assembly above, while the other ring joins with a ring of a CFU of the planar assembly below.

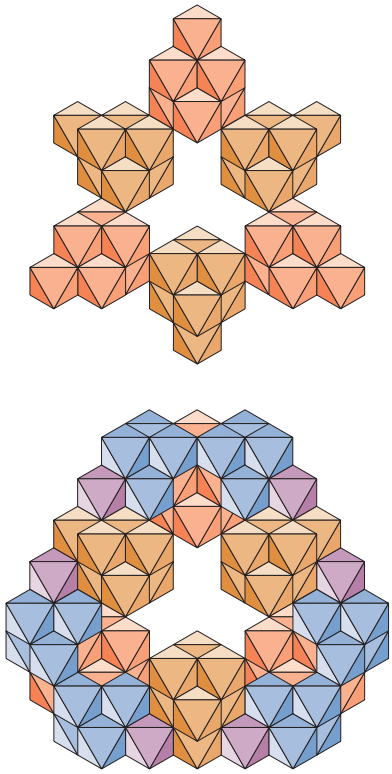
$6SiO_2$ rings

Type I



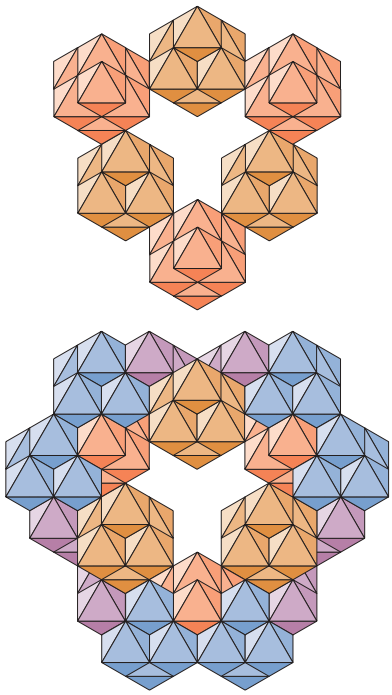
Ring of six silica groups, Type I.
The ring is composed of two sets of three silica groups each. The groups of each set are identical except for a rotation of one-third revolution about the viewing direction. The Si-atoms of the set at the top of the figure have their Si-octas uppermost and the orientation of one O-atom orientations is the mirror of the other; they are colored blue. The other set is in the middle and the Si-octas of these Si-atoms is lowermost, they are colored violet. The silica groups are connected by a double-clefted join between their O-atoms.

Type II



Ring of six silica groups, Type II
The Si-atoms are shown at the top as they are positioned in the ring. There are two sets of three each which are colored red or orange. The red colored Si-atoms have their 456-faces uppermost; the orange colored have their 123-faces uppermost. Within each set the orientations differ by a third of a revolution about the viewing direction. The O-atoms of each silica group have the same orientation. The O-atoms of adjoining groups are cleftly joined.

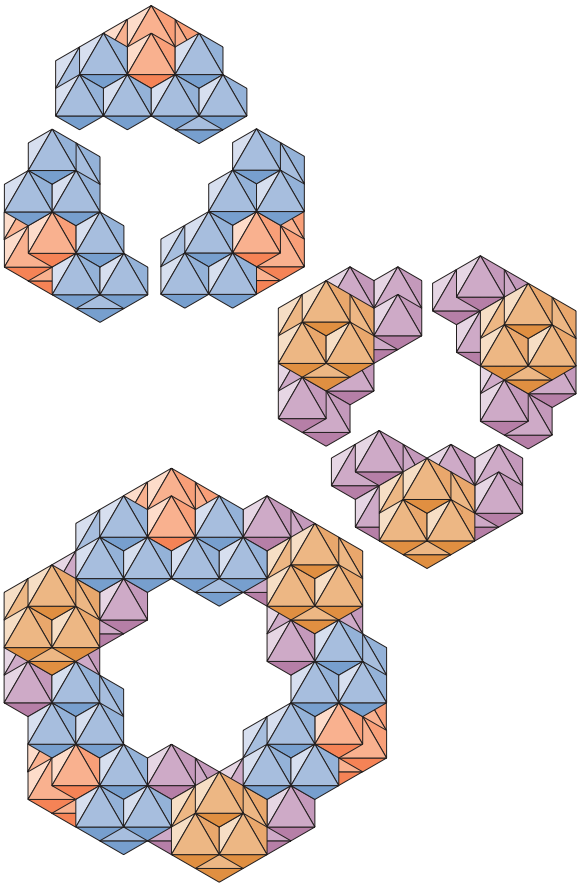
Type III



Ring of six silica groups, Type III

The top shows the relationship of the six Si-atoms of the ring. The red colored atoms differ from the orange colored atoms by a rotation of one-half revolution about the bottom edge of the page. The O-atoms of each group have the same orientation. The O-atoms of adjoining groups are cleftly joined.

Type IV

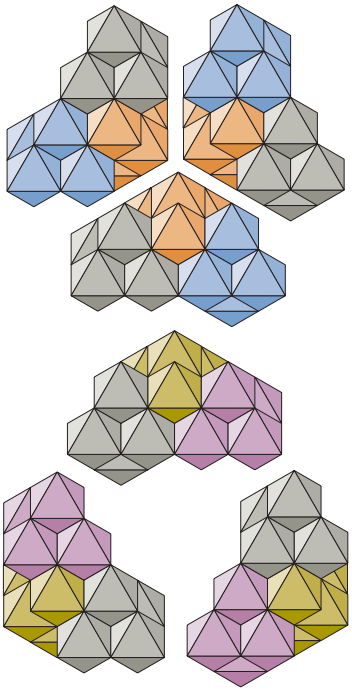


Ring of six silica groups, Type IV

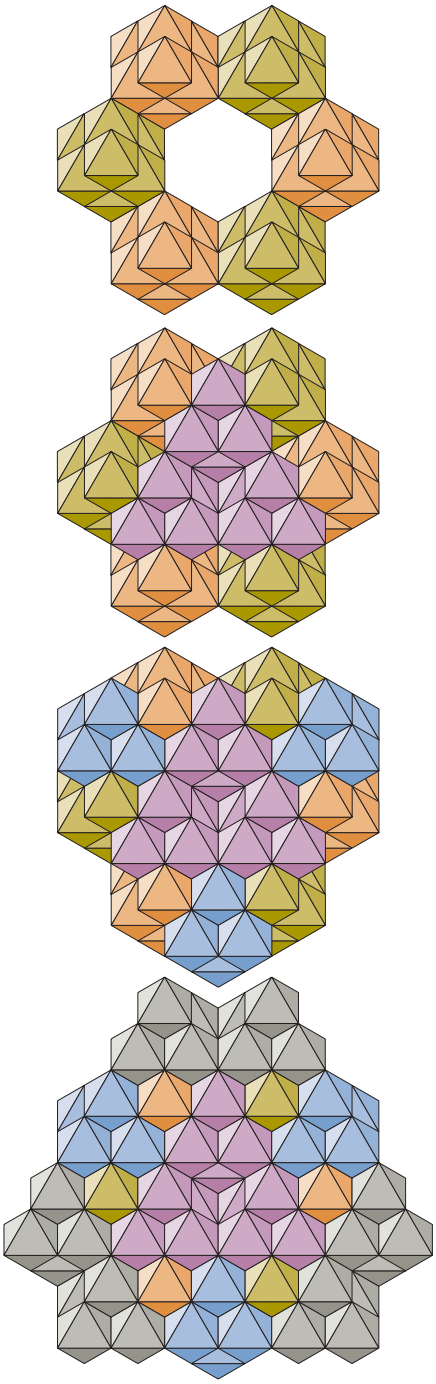
The two sets of three silica groups which form the ring are shown above it. The Si-atoms of each set are inverted relative to the other set. The O-atoms of the silica groups of each set are oppositely directed. Those of the top set are ccw; those colored violet are cw.

Type V

The figure on the right shows the arrangement of the atoms of a fifth type of ring composed of six silica groups. At the top of the figure, the relationship of the six Si-atoms is shown. They have a common orientation. Below them, the three O-atoms which are central are added. They are colored violet. Three more O-atoms are added which are colored blue in the next view. Each of the six O-atoms which have been added thus far are cleftly joined to adjacent Si-atoms. There remains one unoccupied cleft for each Si-atom. These clefts are filled with the six O-atoms which are colored gray that have been added at the bottom of the figure. These last O-atoms are used to join ring to ring.

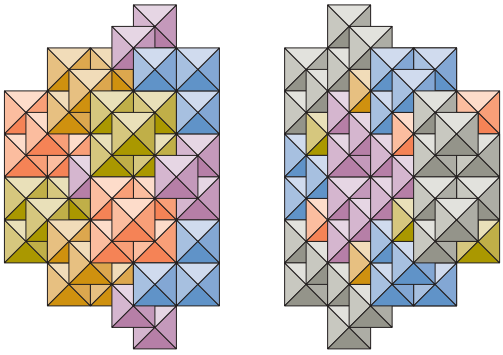


Silica groups of the Type V ring.
The figure shows how the O-atoms might be assigned to the silica groups. Each Si-atom has one O-atom which joins with another Si-atom to form the ring and another O-atom which is used for ring-to-ring joining.

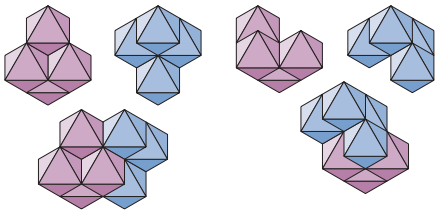


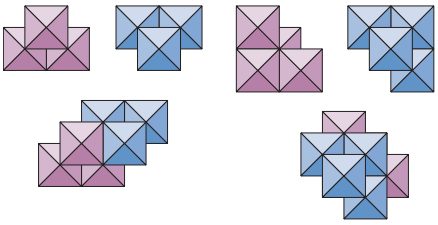
Ring of six silica groups, Type V
The Type V silica ring is characterized by having O-atoms available for external joins. They are colored gray.

Fourfold ring of type V rings

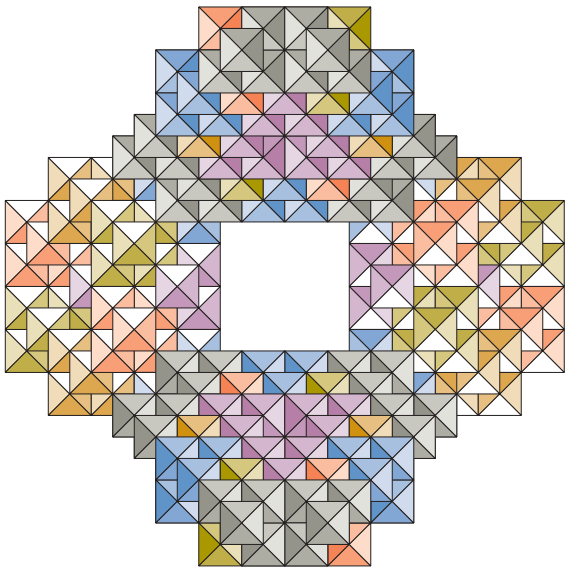


Vertexial views of the Type V ring. One side of the ring is defined by the 143-faces of the Si-atoms, the other side is defined by three he-octas of each O-atom and the Si-octa of the Si-atoms.



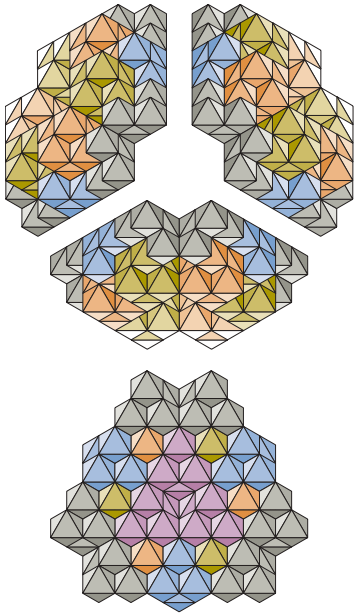


Double cleftly joined O-atoms. Two O-atoms are shown cleftly joined in each of two assemblies. This is the join between the Type V $6SiO_2$ rings.

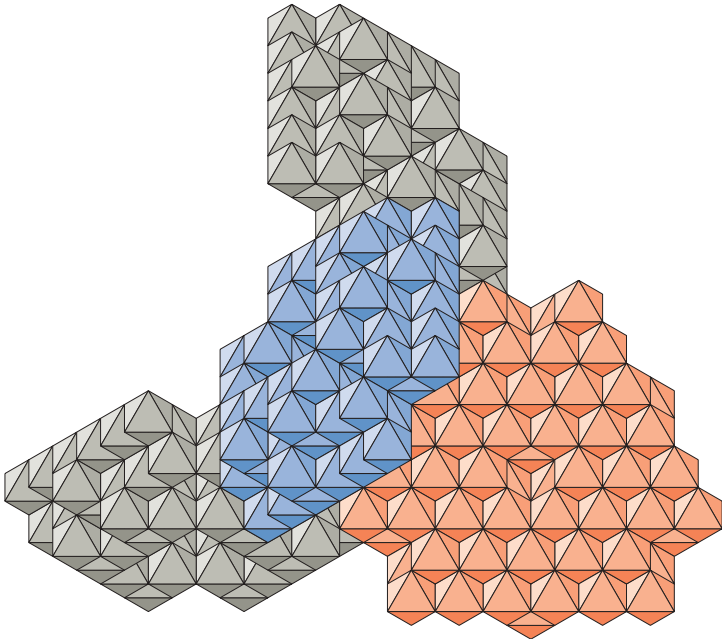


Type V tetrahedral assembly

This is a ring of rings which are linked by double cleftly joined O-atom pairs. The four rings are in the four possible orientations for the facially planar rings

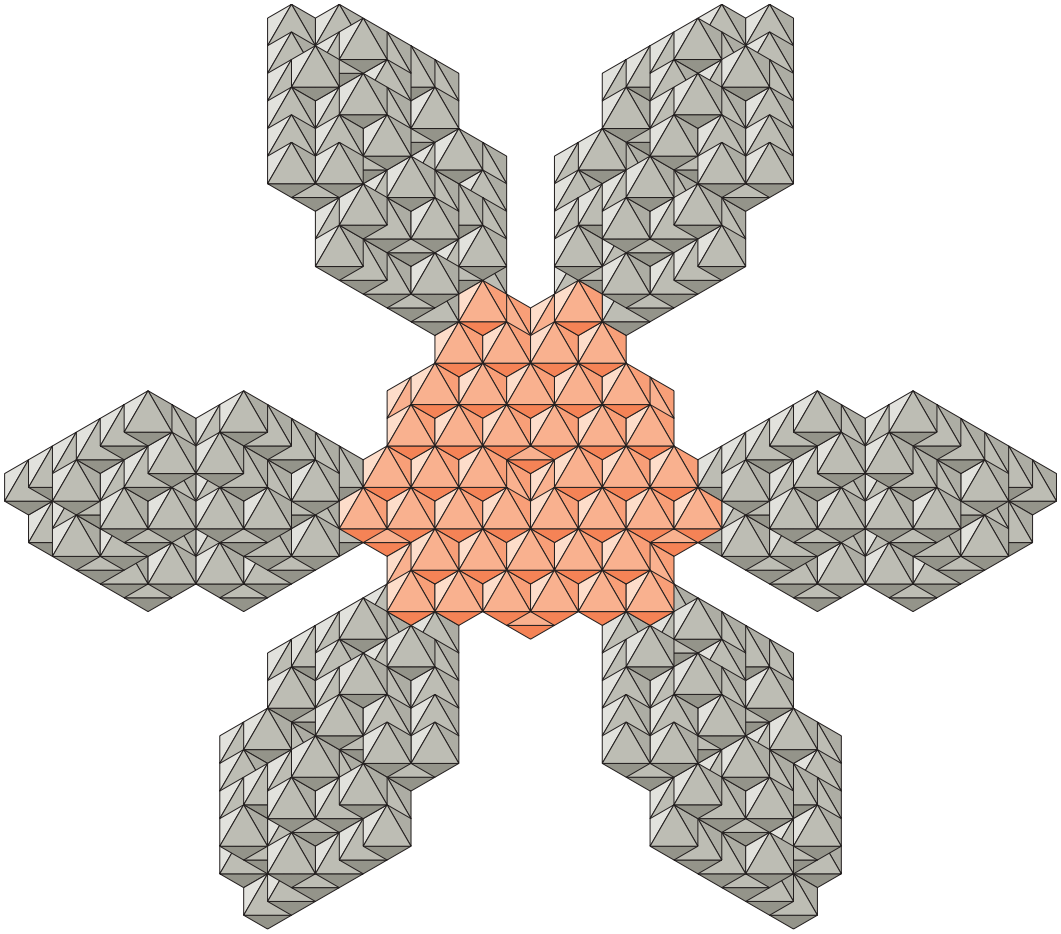


Four facial orientations of the Type V ring.



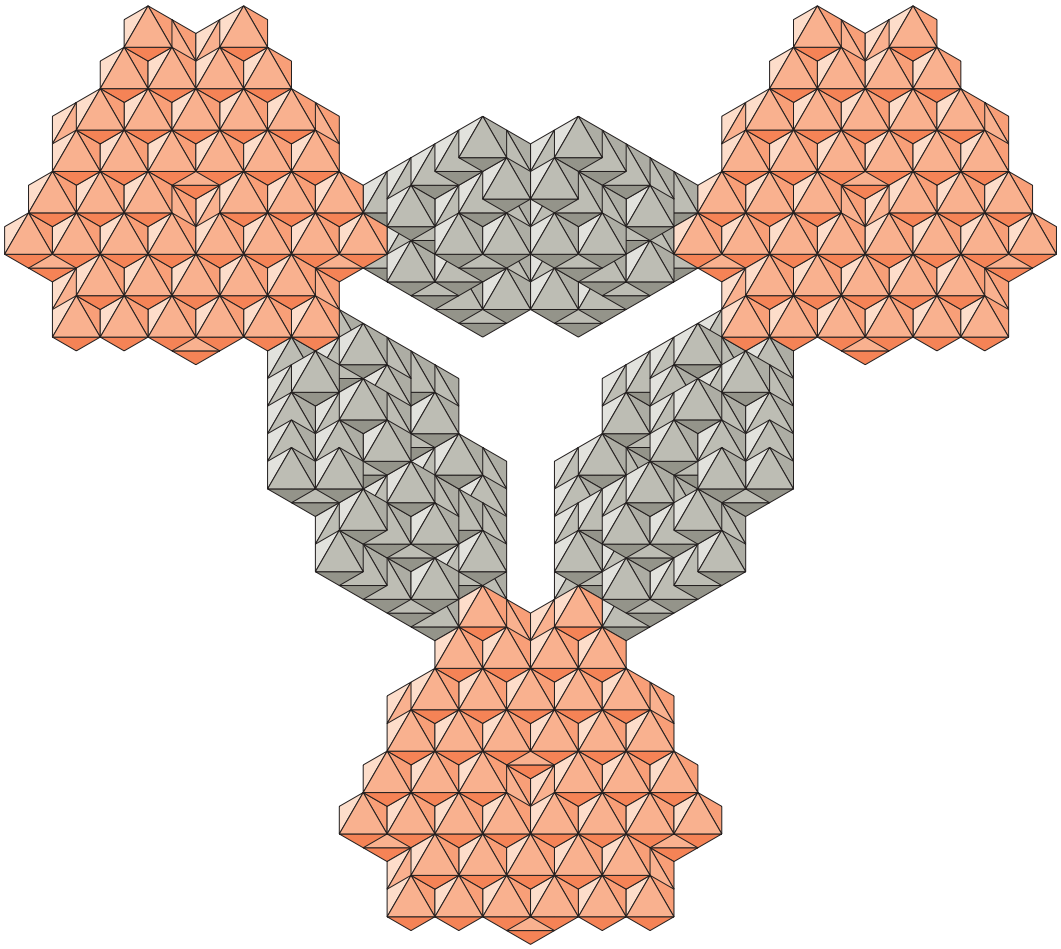
Tetrahedral assembly of Type V rings viewed facially.

Type V crystal, symmetry center type A



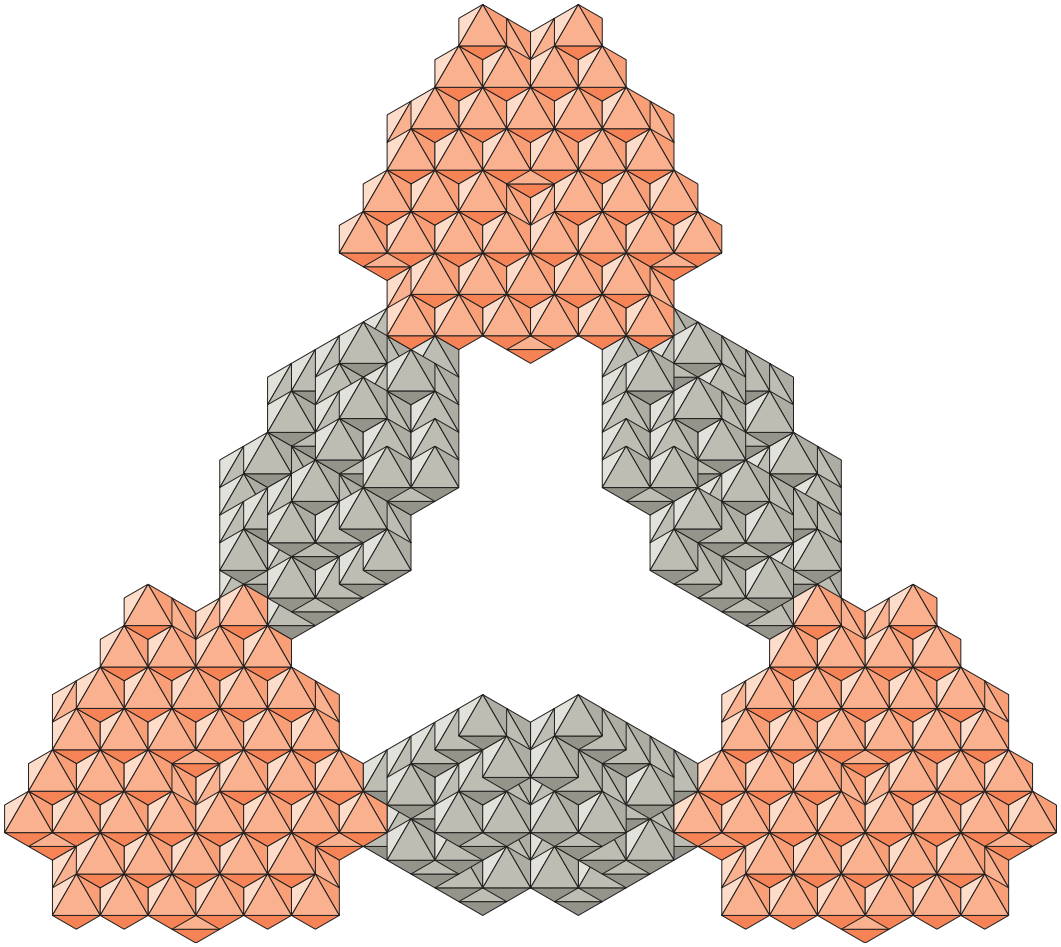
Symmetry center Type A, crystal of Type V rings.

Type V crystal, symmetry center type B



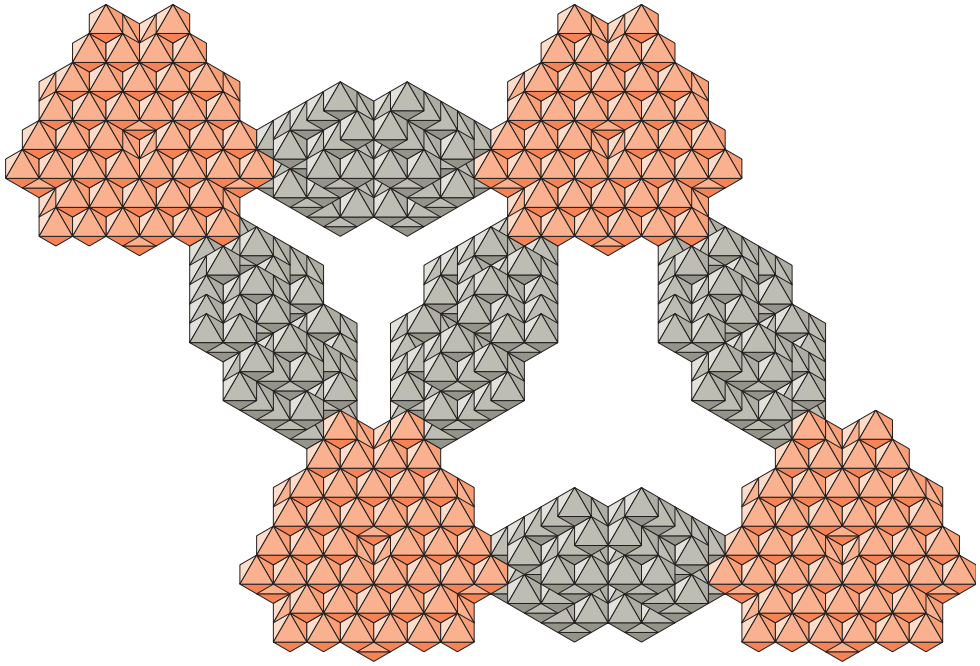
Symmetry center Type B, crystal of Type V rings.

Type V crystal, symmetry center type C



Symmetry center Type C, crystal of Type V rings.

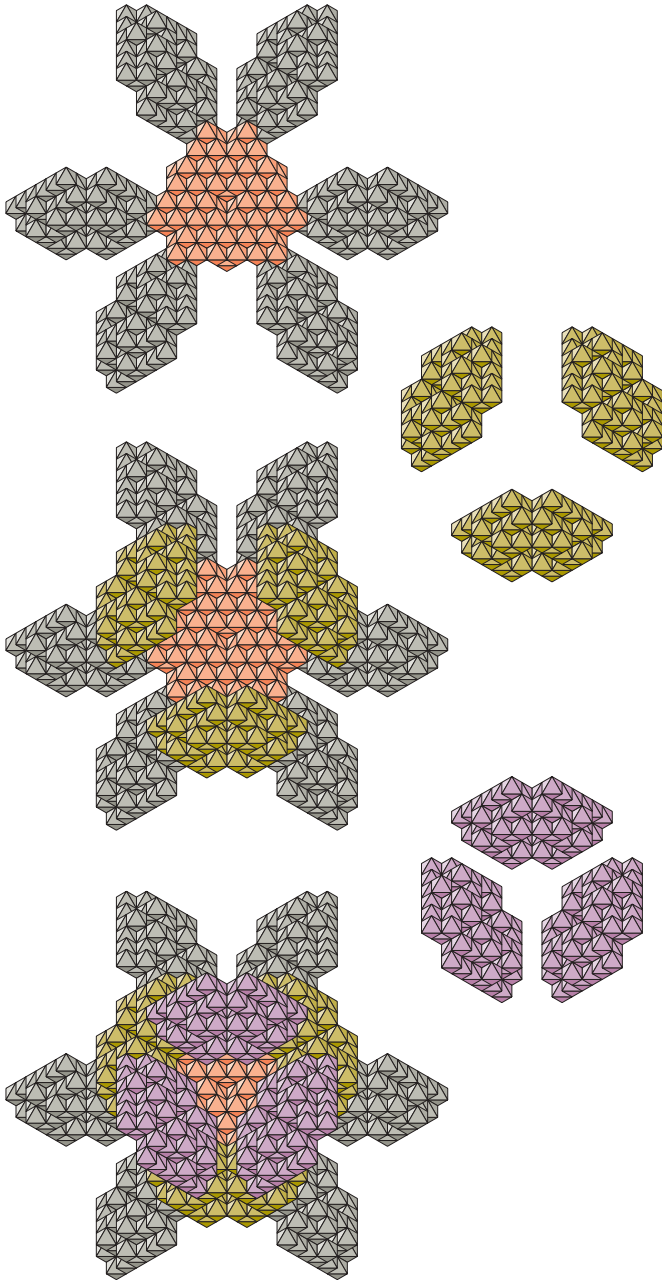
Type V crystal, symmetry centers B & C



Adjoining symmetry centers Types B and C

.This figure shows two contiguous centers of symmetry. Each of the horizontal rings (colored red) is the hub of the third type of symmetry center.

Type V crystal, symmetry center stack



The figure shows how the three centers of symmetry are stacked one above the other in turn.

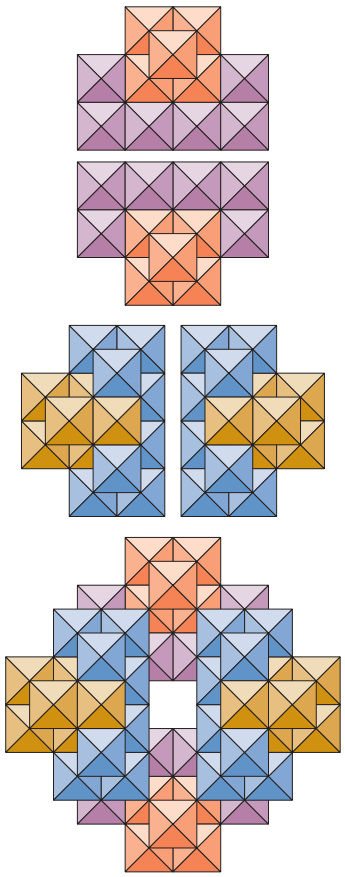
A unit composed of the type 1 center of symmetry with 3 adjacent spokes removed can form the plane with translations in three join directions at 60°. A structural stack of three such units is a cfu.

The rings are identical and identically joined to six other rings none of which has the same orientation as the hub. The others have three orientations between them, two rings per orientation.

The rings with the same orientation are at 180°. The orientations are parallel to the four pairs of faces of the regular octahedron. The rings of the same orientation establish with the hub a chain which continues in either direction. The chain directions are parallel to the edgial diameters of the regular octahedron.

Vertexial SiO_2 rings

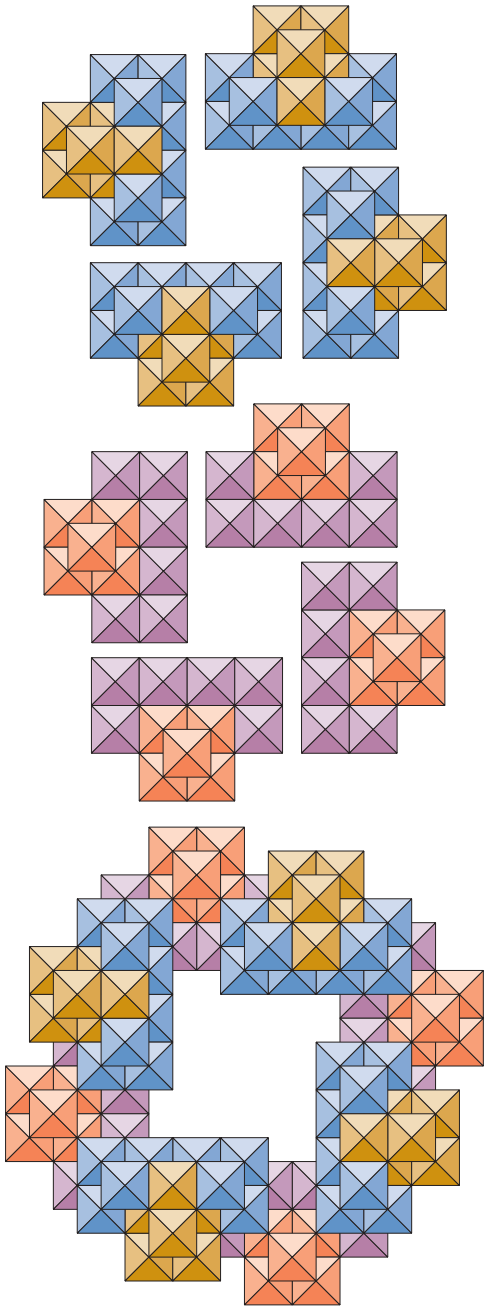
4SiO2 ring



$4SiO_2$ ring

This ring is composed of two pairs of SiO_2. Each Si has one cw O-atom and one ccw O-atom and one SiO_2 is inverted with respect to the other.

8SiO2 ring

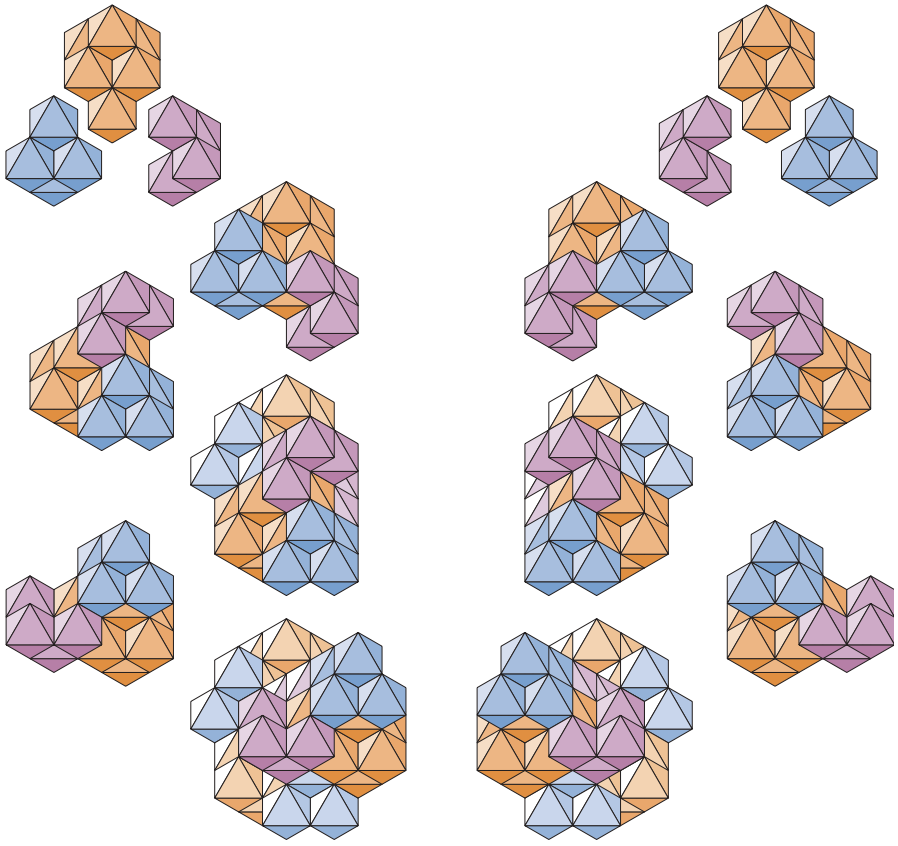


$8SiO_2$ ring

This ring is composed 4 pairs of mixed O-atom SiO_2.

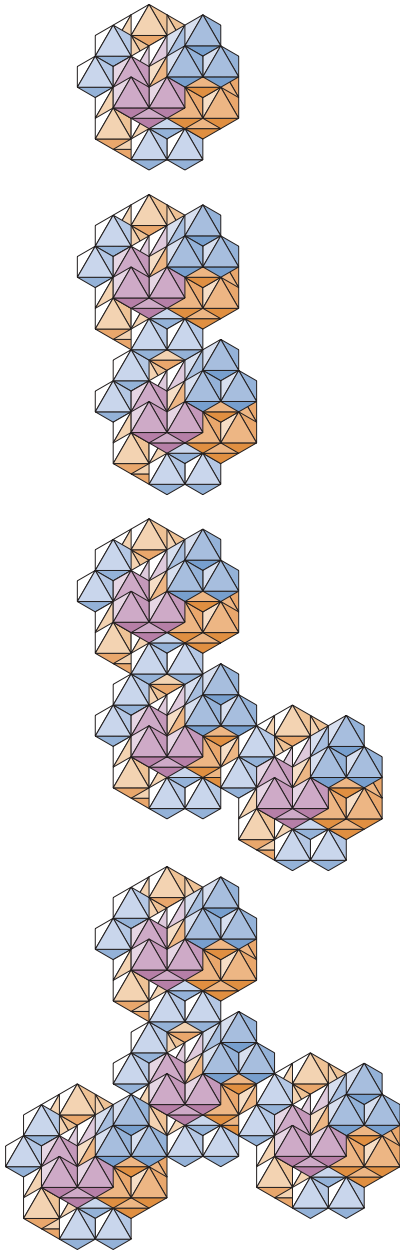
SiO_2 helixes

Silica groups can form helixes. In the following figure are depicted two silica helixes and the units which form them. The adjacent Si-atoms are connected by an O-atom. Each helix mirrors the other. The one on the left is clockwise toward; the one on the right is counterclockwise toward. The second O-atom of each unit is available for joining each of the silica groups of the helix to other groups. The helixes are viewed axially, from opposite directions, and each is a single turn.

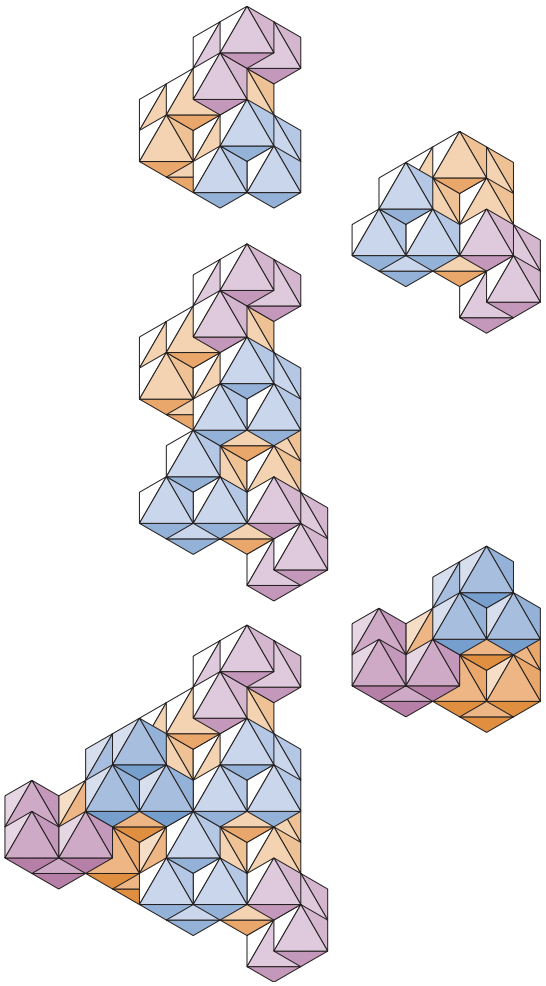


Two SiO_2 helixes, cw and ccw, toward, Type A.

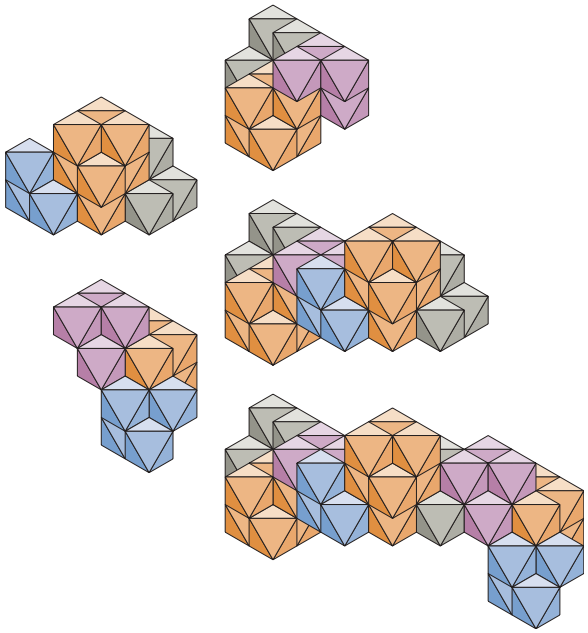
The helical axis is facial and in its direction relative to the Si-atom is **456**, **125**, or **236**. Just one O-atom of each silica group is used for the intrahelical join.



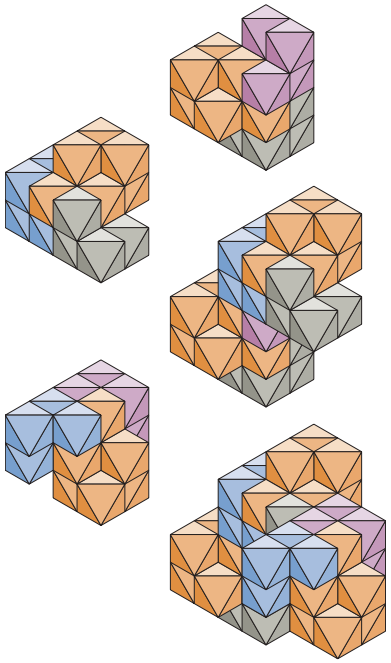
Joins between cw-toward Type A helixes.
The C-octa of a Si-atom of one helix occupies a void of an O-atom of an adjoining helix.



Detail of the interhelical join between three cw-toward Type A helixes.
Each of the three silica groups which join to form the assembly at the bottom of the figure belong to a different helix. Each group is rotated one-third of a revolution with respect to the other two.



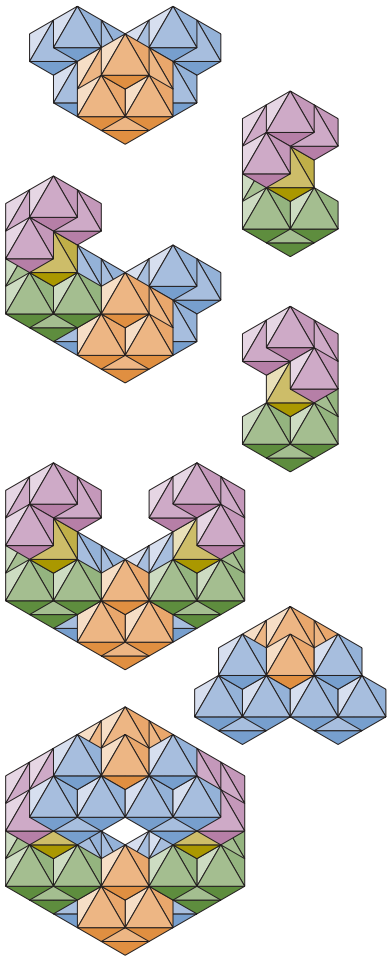
SiO_2 helix Type B, oblique view.



SiO_2 helix Type B, axial view.

The helical axis is facial and in the direction relative to the Si-atom **456**, **125**, or **236**. The intrahelical join is between an O-atom of a silica group and an O-atom of an adjoining silica group.

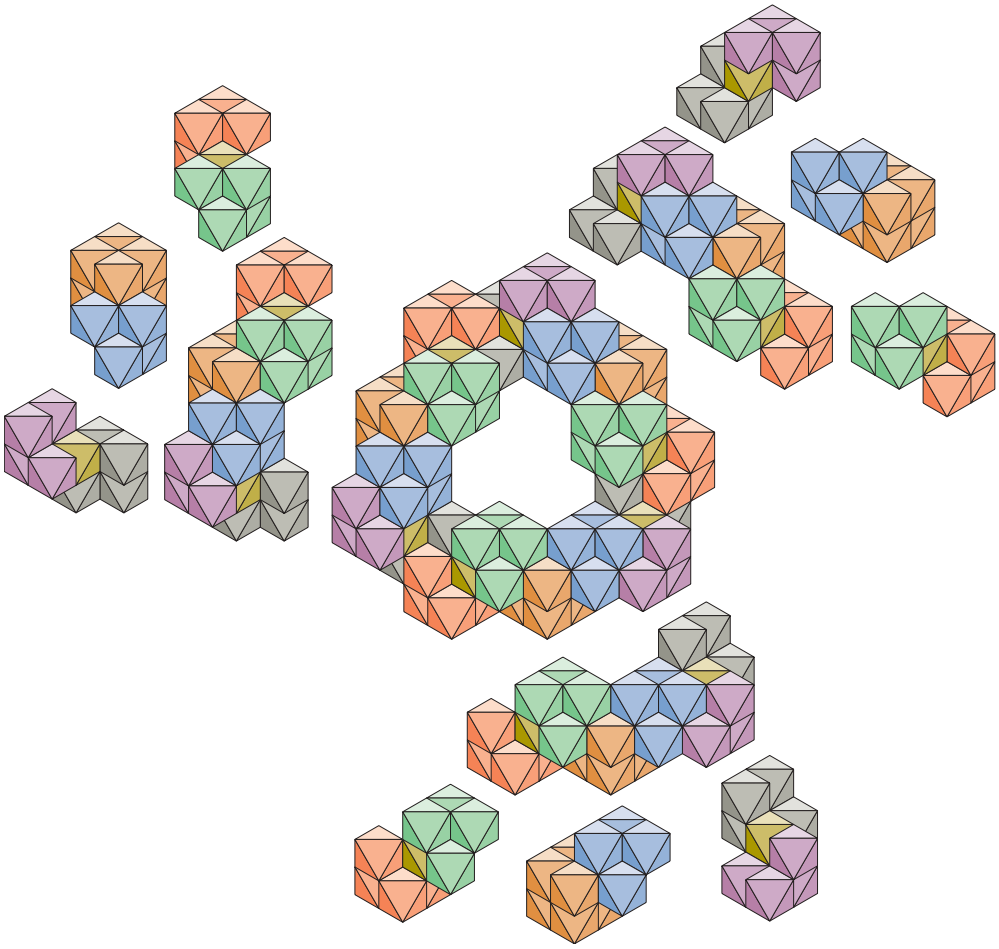
Silica groups linked by H_2O pairs **$2[SiO_2 \bullet (H_2O)_2]$ ring**



Two silica groups linked by paired H_2O groups.

The figure shows the assembly of a ring composed of two silica groups linked by two paired H_2O groups. The top group is a silica group with the Si-atom colored orange. The assembly commences with the addition of paired H2O groups and terminates with the addition of the second silica group.

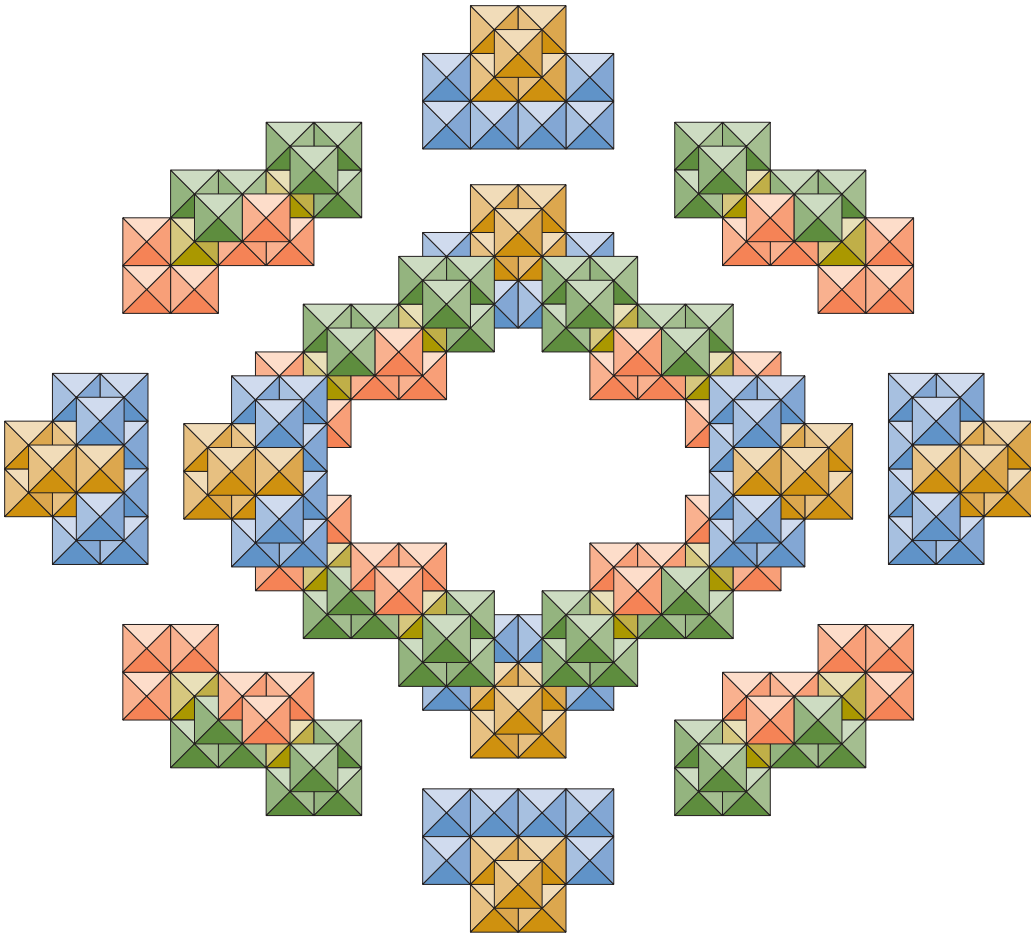
$3[SiO_2 \bullet 2(H_2O)_2]$ ring



Three silica groups linked by two paired H_2O groups.

The completed ring is at the center of the figure. Just outward from the assembly are the three identical subassemblies which produce the ring. The components of the subassemblies form the outermost groups. Each of the silica groups is depicted without one of its two O-atoms which fits in the remaining cleft of the Si-atom

$4[SiO_2 \bullet (H_2O)_2]$ ring



Four silica groups linked by two paired H_2O groups.

The completed ring lies at the center of the figure. It is surrounded by the four silica groups and the four paired H_2O groups which constitute it.