Si-O distances in some silicates containing fluor ions

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In fluor-tremolite, fluor-phlogopite and topaz, the Si-O distances, where the oxygens are bonded to the non-tetrahedral ions containing fluor ions, are longer in comparison with those in no-fluorine compounds. This is caused from the decreasing of the π bonding between silicon and oxygen affected by the electronegative fluor ion.

Introduction

Fluorine is the most electronegative element and bonded to the non-tetrahedral cations in some silicates. To study the correlation between the Si-O distances and the electronegativities of the substituents on the silicon atom, the Si-O distances in some silicates containing fluor ions have been examined.

Si-O distances in hydroxyl- and fluor-tremolites

The basic structure of tremolite was determined by Warren (1929). Fig. 1 shows the structure projected along *c*. The M(1)-, M(2)- and M(3)- octahedra are occupied by magnesium, the M(4)- tetragonal antiprism by calcium, the T(1)- and T(2)-tetrahedra by silicon, and the A site is vacant. The crystal structures of a hydroxyl-tremolite $\{Ca_2Mg_5Si_8O_{22}(OH)_2\}$ and a fluor-tremolite $(Ca_2Mg_5Si_8O_{22}F_2)$ have been refined by Papike, Ross and Clark (1969) and Cameron and Gibbs (1973), respectively. Each Si-O distance is listed in Table 1.

The T(1)-O(1) distance in fluor-tremolite is significantly longer than that in hydroxyl-tremolite. On the other hand, the T(2)-O(2) distance in fluor-tremolite is only

Fig. 1. The structure of tremolite projected along *c*.

Table 1. Si-O distances (Å) in hydroxyl and fluor-tremolites

	hydroxyl- tremolite *	fluor- tremolite **
T(1)-O(1)	1.602(2)	1.614(3)
O(5)	1.632(2)	1.628(3)
O(6)	1.629(2)	1.630(4)
O(7)	1.616(1)	1.606(2)
T(2)-O(2)	1.616(2)	1.623(3)
O(4)	1.586(2)	1.587(3)
O(5)	1.653(2)	1.648(4)
O(6)	1.672(2)	1.659(3)

*Papike, Ross and Clark(1969)

**Cameron and Gibbs(1973)

slightly longer than that in hydroxyl-tremolite. Cameron and Gibbs (1973) described that the significantly longer T(1)-O(1) distance in fluor-tremolite may be explained as a necessary geometrical adjustment of the structure to accommodate the smaller M(1)- octahedron and the slightly longer T(2)-O(2) distance in fluor-tremolite may be the result of articulation requirements between the tetrahedral and octahedral layers.

However, it is possible to consider that the elongations in fluor-tremolite are caused from the electronegativities of the non-tetrahedral ions containing fluor ions. In hydroxyl-tremolite, the O(1) is coordinated by one Si, two $\text{MgO}_3(\text{OH})_2$ and one MgO_5 , and the O(2) by one Si, one $\text{MgO}_3(\text{OH})_2$, one MgO_5 and one CaO_7 . Therefore, the Si-O(1) distance is much affected by the substitution of F for OH than the Si-O(2) distance. Indeed, by the substitution of F for OH, the Si-O(1) distance becomes 0.012 Å longer and the Si-O(2) distance becomes 0.007 Å longer. These elongations may be caused from the decreasing of the π bonding between the Si{T(1) and T(2)} and the O{O(1) and O(2)}.

It is generally found that Si-O distances are shorter when the other substituents on the silicon atom are more electronegative (Ohashi, 1981). These tendencies can be observed in tremolites. That is, by the substitution of F for OH, the mean of the T(1)-O(5, 6 and 7) distances changes from 1.626 Å to 1.621 Å, and the mean of the T(2)-O(4, 5 and 6) distances changes from 1.637 Å to 1.631 Å.

Si, Al-O distances in phlogopites

The basic structure of mica was determined almost simultaneously by Pauling (1930) and Jackson and West (1930). Fig. 2

Fig. 2. The structure of mica projected on the (010) plane.

shows the projection of the structure of Mg-phlogopite on the (010) plane. The apical oxygen(O3) is bonded to three Mg ions and one Si(Al) ion. The Mg ion is bonded to four apical oxygens and two fluor or hydroxyl ions. The basal oxygens (O1, O2 and O2') are bonded two K ions and two Si(Al) ions, respectively. The crystal structures of a natural phlogopite $\{(\text{K}_{0.77}\text{Na}_{0.16}\text{Ba}_{0.05})\text{Mg}_{3.00}\text{Al}_{1.05}\text{Si}_{2.95}\text{O}_{10.00}(\text{F}_{1.30}\text{OH}_{0.70})\}$ and a synthetic fluor-phlogopite $\{\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}\text{F}_2\}$ have been refined by Hazen and Burnham (1973) and Takeda and Morosin (1975), respectively. Each Si(Al)-O distance is listed in Table 2.

Table 2. Si(Al)-O distances (Å) in phlogopites

	natural phlogopite *	fluor phlogopite **
T-O(1)	1.648(2)	1.647(2)
O(1)	1.651(1)	1.650(2)
O(2)	1.6503(9)	1.650(1)
O(3)	1.648(1)	1.656(2)

*Hazen and Burnham(1973)

**Takeda and Morosin(1975)

Although the substitution of OH for F in the natural phlogopite is 35 mol%, the changes in the Si(Al)-O distances can be observed as in tremolites. The Si(Al)-O(3) distance in the natural phlogopite is shorter than that in the fluor-phlogopite. The shortness may be caused from the increas-

ing of the π bonding between the Si(Al) and the apical oxygen (O3) with increasing the hydroxyl ions.

Si-O distances in topaz

The basic structure of topaz was determined independently by Pauling (1928) and Alston and West (1928) and the refinement was carried out by Ladell (1965). Oxygen in topaz is coordinated by one Si and two Al as shown in Fig. 3. The mean of the Si-O distances is 1.641 Å (Ribbe and Gibbs, 1971). This is about 0.02 Å longer than that expected for Si bonded to a three-coordinated oxygen (Brown and Gibbs, 1969). In andalusite and kyanite, which also have three coordinated oxygens and SiO_4 tetrahedra with no shared edges, the mean Si-O distances are 1.628 Å, respectively (Burnham and Buerger, 1961; Burnham, 1963). The mean of the Si-O distances in topaz is unusually long in comparison with those in the two aluminum silicates.

◎ FLUORINE

Fig. 3. The structure of topaz projected on the (010) plane.

In many silicates, the variations in the individual Si-O distances are strongly correlated with the Pauling bond strength received by the oxygen atoms (Baur, 1971). However, such a correlation can not be

found in andalusite. In andalusite structure the silicate tetrahedra are isolated and there are three non-equivalent oxygens (O_b , O_c and O_d). O_b , O_c and O_d oxygens are coordinated by one Si and two $\text{Al}(1)\text{O}_5$, one Si and two $\text{Al}(2)\text{O}_4$, and one Si, one $\text{Al}(1)\text{O}_5$ and one $\text{Al}(2)\text{O}_4$, respectively (Burnham and Buerger, 1961). $\text{Al}(1)\text{O}_5$ is more electronegative than $\text{Al}(2)\text{O}_4$. In andalusite the Si-O distance increases with increasing the sum of the electronegativities of the substituents as listed in Table 3.

Table 3. The Si-O distances and the substituents on the oxygen atoms in andalusite

	distance (Å) *	substituents
Si-O _b	1.635 (5)	Al (1)O ₅ [2x], Si
O _c	1.615 (6)	Al (2)O ₄ [2x], Si
O _d [2x]	1.631 (4)	Al (1)O ₅ , Al (2)O ₄ , Si

*Burnham and Buerger (1961)

In topaz structure the silicate tetrahedra are isolated and there are three non-equivalent oxygens. Each oxygen is coordinated by two AlO_3F_2 and one Si. AlO_3F_2 is more electronegative than AlO_5 . The long Si-O distances in topaz (1.641 Å) may be caused from the electronegative AlO_3F_2 and the π bonding between silicon and oxygen may be weak in comparison with those in andalusite.

It is found that Si-O distances are shorter when the other substituents on the silicon atom are more electronegative (Ohashi, 1981). In $\text{M}_3^{2+}\text{Al}_2\text{Si}_3\text{O}_{12}$ garnet, oxygen is coordinated by two M^{2+} , one Al and one Si, and each Si-O distance decreases with increasing the electronegativity of the M^{2+} cation as two separate trends (Ohashi, 1980; Ohashi, Fujita and Osawa, 1981). In $\text{M}_3^{2+}\text{Al}_2\text{Si}_3\text{O}_{12}$ garnet the bond elongation caused from the decreasing of the π bonding between silicon and oxygen may be smaller than the bond shortening caused

from the increasing of the electronegativities of the substituents bonded to the other three oxygens. On the other hand, the oxygens in topaz are coordinated by three atoms and the mean of the Si-O distances is unusually long (1.641 Å). This may be caused from the large bond elongation and the small bond shortening affected by the electronegative AlO_3F_2 .

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弗素イオンを含む数種の珪酸塩における Si-O 距離

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弗素は最も電気陰性度の高い元素であり、ある種の珪酸塩において修飾イオンと結合している。Si-O 距離と珪素に結合する置換体の電気陰性度との関係を明らかにするために、弗素イオンを含む珪酸塩における Si-O 距離について検討した。透閃石、金雲母及び黄玉においては、弗素と結合する修飾イオンが配位する酸素と珪素との距離は、弗素を含まない場合に比べて長いことが明らかになった。これは電気陰性な弗素により珪素と酸素との間の π 結合が減少するためである。