STUDIES ON THE Si-O DISTANCES IN NaM$^{3+}$Si$_2$O$_6$ PYROXENES

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The dependence of the Si-O distances on the electronegativity, the electronic structure and the size of the non-tetrahedral cations has been re-examined for NaM$^{3+}$Si$_2$O$_6$ pyroxenes. In the Sc-V-Al series the difference, $\Delta_{br-\text{mean}}$, decreases with increasing the electronegativity and the difference, $\Delta_{nbr-\text{mean}}$, increases with increasing the electronegativity, where the $\Delta$mean is the difference between the mean of the four Si-O distances in NaAlSi$_2$O$_6$ pyroxene and that in NaM$^{3+}$Si$_2$O$_6$ pyroxene, and $\Delta_{br-\text{mean}}$ is the difference between the mean of the Si-O (br) distances and the $\Delta$mean. In the Cr-In-Fe series the mean of the Si-O (nbr) distances increases with increasing the electronegativity and the difference, $\Delta_{br-\text{mean}}$, decreases with increasing the electronegativity.

The mean of the four Si-O distances in NaM$^{3+}$Si$_2$O$_6$ pyroxene depends on the size of the cation occupying the M1 site (Ohashi, Fujita and Ii, 1979). Each Si-O distance is however strongly influenced by not only the electronegativity of the M$^{3+}$ cations but also their electronic structures (Ohashi, 1979). The difference between the mean of the Si-O (bridging: br) distances and the mean of the Si-O (non-bridging: nbr) distances decreases with increasing the electronegativity of the M$^{3+}$ cation and two groups of variation trend are observed. One group is the Sc-V-Al series and the other is the Cr-In-Fe series. The purpose of this study is to re-examine the dependence of the Si-O distances on the electronegativity, the electronic structure and the size of the non-tetrahedral cation for NaM$^{3+}$Si$_2$O$_6$ pyroxene.

The structural data of NaInSi$_2$O$_6$ pyroxene reported by Christensen and Hazell (1967) and referred by Ohashi (1979) include the relatively large estimated standard errors. Hawthorne and Grundy (1974)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Si-O1</th>
<th>Si-O2</th>
<th>mean</th>
<th>Si-O3A1</th>
<th>Si-O3A2</th>
<th>mean,</th>
<th>mean of</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAlSi$_2$O$_6$</td>
<td>1.637(2)</td>
<td>1.590(2)</td>
<td>1.613</td>
<td>1.628(2)</td>
<td>1.636(2)</td>
<td>1.632</td>
<td>1.623</td>
</tr>
<tr>
<td>NaCrSi$_2$O$_6$</td>
<td>1.626(4)</td>
<td>1.586(3)</td>
<td>1.606</td>
<td>1.640(4)</td>
<td>1.645(4)</td>
<td>1.642</td>
<td>1.624</td>
</tr>
<tr>
<td>NaVSi$_2$O$_6$</td>
<td>1.624(2)</td>
<td>1.593(2)</td>
<td>1.609</td>
<td>1.630(2)</td>
<td>1.648(2)</td>
<td>1.639</td>
<td>1.624</td>
</tr>
<tr>
<td>NaFeSi$_2$O$_6$</td>
<td>1.629(2)</td>
<td>1.598(2)</td>
<td>1.614</td>
<td>1.637(2)</td>
<td>1.646(2)</td>
<td>1.642</td>
<td>1.628</td>
</tr>
<tr>
<td>NaMnSi$_2$O$_6$</td>
<td>1.630(3)</td>
<td>1.592(2)</td>
<td>1.611</td>
<td>1.653(2)</td>
<td>1.653(3)</td>
<td>1.653</td>
<td>1.632</td>
</tr>
<tr>
<td>NaInSi$_2$O$_6$</td>
<td>1.632(3)</td>
<td>1.592(2)</td>
<td>1.612</td>
<td>1.649(3)</td>
<td>1.655(3)</td>
<td>1.652</td>
<td>1.632</td>
</tr>
</tbody>
</table>


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Si-O distances in NaM$^{3+}$Si$_2$O$_6$ pyroxenes

more than one empty 3d orbital in the t$_{2g}$ state. In the Cr-In-Fe series, the mean of the Si-O (nbr) distances increases with increasing the electronegativity of the M$^{3+}$ cation. The numbers of 3d electrons of the M$^{3+}$ cations in the Cr-In-Fe series are 3, 10 and 5, respectively. The three 3d electrons of Cr$^{3+}$ ion occupy the 3d orbitals in the t$_{2g}$ state. In Cr-In-Fe series, the octahedral sites are occupied by the M$^{3+}$ cations which have no empty 3d orbital in the t$_{2g}$ state.

refined the crystal structure of NaInSi$_2$O$_6$ pyroxene. The each Si-O distance is listed in Table 1 with the data of the other NaM$^{3+}$Si$_2$O$_6$ pyroxenes. Although the mean of the four Si-O distances in NaInSi$_2$O$_6$ pyroxene is in agreement with that reported by Christensen and Hazell (1967), the each bond distance is not the same. The variations of the mean of the Si-O (br) distances and the mean of the Si-O (nbr) distances with the electronegativity of the M$^{3+}$ cation are shown in Figure 1. In the Sc-V-Al series, the mean of the Si-O (br) distances decreases with increasing the electronegativity of the M$^{3+}$ cation. The numbers of 3d electrons of the M$^{3+}$ cations in the Sc-V-Al series are 0, 2 and 0, respectively. The M$^{3+}$ cation occupies the octahedral site in the pyroxene structure. The two 3d electrons of V$^{3+}$ ion occupy the 3d orbitals in the t$_{2g}$ state. There is an empty 3d orbital in the t$_{2g}$ state. In the Sc-V-Al series, the octahedral sites are occupied by the M$^{3+}$ cations which have

The differences, $\Delta$br-nbr, between the mean of the Si-O (br) distances and the mean of the Si-O (nbr) distances are listed in Table 2 with the electronegativities of the M$^{3+}$ cations. Their variation is shown in Figure 2. The differences, $\Delta$br-nbr, in the Sc-V-Al series correlate with the electronegativities of the M$^{3+}$ cations as pointed out by Ohashi (1979). However, the plots representing Cr, In and Fe are scattered, affected by other factors.

The mean of the four Si-O distances in NaM$^{3+}$Si$_2$O$_6$ pyroxene depends on the size of the M$^{3+}$ cation (Ohashi, Fujita and Ii, 1979). Assuming that in the Sc-V-Al series

Fig. 1. The Si-O distances plotted against the electronegativities of the M$^{3+}$ cations for six NaM$^{3+}$Si$_2$O$_6$ pyroxenes. Open circle represents the mean of the four Si-O distances and the associated vertical line connects the mean of the Si-O (br) distances and the mean of the Si-O (nbr) distances.

Fig. 2. The differences, $\Delta$br-nbr, between the mean of the Si-O (br) distances and the mean of the Si-O (nbr) distances plotted against the electronegativities of the M$^{3+}$ cations for six NaM$^{3+}$Si$_2$O$_6$ pyroxenes.
Table 2. The differences (Å), \( \Delta_{br-nbr} \), \( \Delta_{mean} \), 
\( \Delta_{br-\Delta_{mean}} \), \( \Delta_{nbr-\Delta_{mean}} \) and \( \Delta_{br-2\Delta_{mean}} \)
in NaM\textsuperscript{3+}Si\textsubscript{2}O\textsubscript{6} pyroxenes and the 
electronegativities of the M\textsuperscript{3+} cations 

\begin{tabular}{|c|cccc|}
\hline
Crystal & \( \Delta_{br-nbr} \) & \( \Delta_{mean} \) & \( \Delta_{nbr-\Delta_{mean}} \) & \( \Delta_{br-2\Delta_{mean}} \) \\
\hline
NaM\textsubscript{3}Si\textsubscript{2}O\textsubscript{6} & 0.042 & 0.009 & 1.644 & 1.602 & 1.3 \\
NaAlSi\textsubscript{2}O\textsubscript{6} & 0.030 & 0.001 & 1.636 & 1.610 & 1.5 \\
NaAl\textsubscript{3}Si\textsubscript{2}O\textsubscript{6} & 0.019 & 0 & 1.612 & 1.623 & 1.5 \\
NaFe\textsubscript{3}Si\textsubscript{2}O\textsubscript{6} & 0.036 & 0.001 & 1.640 & 1.6 & 1.6 \\
NaFe\textsubscript{2}Si\textsubscript{2}O\textsubscript{6} & 0.040 & 0.009 & 1.634 & 1.7** & \\
NaFe\textsubscript{2}Si\textsubscript{2}O\textsubscript{6} & 0.028 & 0.005 & 1.652 & 1.8 & \\
\hline
\end{tabular}

* Gordy and Thomas (1956) ** Pauling (1960)

Fig. 3. The differences, \( \Delta_{br-\Delta_{mean}} \), \( \Delta_{nbr-\Delta_{mean}} \), and \( \Delta_{br-2\Delta_{mean}} \), and the mean of the Si-O (nbr) distances plotted against the electronegativities of the M\textsuperscript{3+} cations for NaM\textsuperscript{3+}Si\textsubscript{2}O\textsubscript{6} pyroxenes.

The size of the M\textsuperscript{3+} cation affects on the Si-O (br) distances and the Si-O (nbr) distances, the differences, \( \Delta_{br-\Delta_{mean}} \) and \( \Delta_{nbr-\Delta_{mean}} \), are free from the size of the M\textsuperscript{3+} cation, where the \( \Delta_{mean} \) is the difference between the mean of the four Si-O distances in NaAlSi\textsubscript{2}O\textsubscript{6} pyroxene and that in NaM\textsuperscript{3+}Si\textsubscript{2}O\textsubscript{6} pyroxene, and \( \Delta_{br-\Delta_{mean}} \) is the difference between the mean of the Si-O (br) distances and the \( \Delta_{mean} \). The \( \Delta_{br-\Delta_{mean}} \) and the \( \Delta_{nbr-\Delta_{mean}} \) are listed in Table 2. The variations of the differences, \( \Delta_{br-\Delta_{mean}} \) and \( \Delta_{nbr-\Delta_{mean}} \) with the electronegativities of the M\textsuperscript{3+} cations are shown in Figure 3. The difference, \( \Delta_{br-\Delta_{mean}} \), decreases with increasing the electronegativity.

Table 3. Si-O (br) distances for four disiloxanes and electronegativities of the substituents

<table>
<thead>
<tr>
<th>Compound</th>
<th>Si-O(Å)</th>
<th>( \chi^* )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(SiR\textsubscript{3})\textsubscript{2}</td>
<td>1.634(2) &amp; 2.1 &amp; 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(Si[C\textsubscript{6}H\textsubscript{5}R\textsubscript{3}]\textsubscript{2}</td>
<td>1.618(2) &amp; 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(SiCl\textsubscript{3})\textsubscript{2}</td>
<td>1.592(10) &amp; 3.0 &amp; 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(SiF\textsubscript{3})\textsubscript{2}</td>
<td>1.580(25) &amp; 4.0 &amp; 4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Fig. 4. The Si-O distances plotted against the electronegativities of the substituents for four disiloxanes.

The Si-O-Si bond in pyroxene structure is disturbed by some factors. One of them is the size of the M\textsuperscript{3+} cation. On the other hand, the Si-O-Si bond in the modification of
silicic acid is less disturbed. The Si-O (br) distances in four disiloxanes are listed in Table 3 with the electronegativities of the substituents. The variation of the Si-O (br) distances with the electronegativities is shown in Figure 4. The Si-O (br) distance decreases with increasing the electronegativity as the $d_{br\text{-}mean}$ and the $d_{br\text{-}2d\text{-}mean}$ in NaM$^{3+}$Si$_2$O$_6$ pyroxenes. It is generally found that Si-X bond lengths are shorter when the other substituents on the silicon atom are more electronegative (Krisher and Pierce, 1960). This is exemplified by the Si-O distances in NaM$^{3+}$Si$_2$O$_6$ pyroxenes and disiloxanes.

The $d_{nbr\text{-}mean}$ in the Sc-V-Al series and the mean of the Si-O ( nbr) distance in the Cr-In-Fe series increase with increasing the electronegativity of the M$^{3+}$ cation. These phenomena may be caused from the decreasing of $\pi$ bonding between Si and O (nbr).

REFERENCES


Ohashi, H., Fujita, T. and Ii, N. (1979), Structure of Ca$_{1.00}$Sc$_{0.84}$Ti$_{0.27}$Al$_{1.16}$Si$_{0.73}$O$_6$ pyroxene. J. Japan. Assoc. Min. Petr. Econ. Geol., 74, 280-286.


NaM$^{3+}$Si$_2$O$_6$輝石におけるSi-O距離に関する研究

大橋 晴夫

NaM$^{3+}$Si$_2$O$_6$輝石におけるSi-O距離の修飾イオンの電気陰性度、電子構造、及び大きさに対する依存性について、再検討した。Sc-V-Al系列においては、電気陰性度の増加とともに$d_{br\text{-}mean}$が減少し、$d_{nbr\text{-}mean}$が増加する。ここで$d_{mean}$は、NaAlSi$_4$O$_8$輝石におけるSi-O距離の平均値と、NaM$^{3+}$Si$_2$O$_6$輝石におけるそれとの差であり、$d_{br\text{-}mean}$は、Si-O(br)距離の平均値と$d_{mean}$との差である。Cr-In-Fe系列においては、電気陰性度の増加とともに、Si-O(nbr)距離の平均値が増加し、$d_{br\text{-}2d\text{-}mean}$が減少する。