A THEORETICAL DISCUSSION ON THE CHEMICAL
CONSTITUTION OF GARNETS AS REVEALED
BY X-RAY INVESTIGATIONS

By N Jayaraman

From the fundamental investigations of Menzer on the crystal
structure of garnets and the later work of Herrsch it can be gathered
that the structure of garnets consists of an oxygen skeleton in the
interspaces of which the metallic ions are packed. As a result of the
above investigations it has been established that all garnets regardless of
their composition and properties have the same crystal structure and
they have the same space group, viz., \( O_{h}^{10} \) space group with the body-
centred lattice of the holohedral class of the cubic system.

Menzer tried to fit in the three space groups, viz., \( T_d^{2}, O_{h}^{3} \) and \( O_{h}^{10} \)
with the structure of garnets, but he rejected \( T_d^{2} \) as it involved a face-
centred lattice. So he selects for discussion only the space groups
\( O_{h}^{3} \) and \( O_{h}^{10} \). Both these space groups are applicable to the garnet
structure as they have a body-centred lattice and both these space
groups possess 16–24–, and 96– number positions. So each unit cell
can accommodate eight molecules of \( R'' R' R_{2} \) \( SiO_{16} \). In the space group
\( O_{h}^{10} \), the type of structural formula proposed by Morozewicz (\( R'' R' 
R_{2} \) \( Si_{2}O_{8} \) \( R'_{2} SiO_{4} \)) is also possible if it is rewritten as follows —

\[
\begin{align*}
R'' & \quad R' \\
8 \quad Si_{2}O_{4} & \quad R'_{2} \\
& \quad R''
\end{align*}
\]

But Menzer discards this formula as it is against the observed
facts, viz., that in the garnet lattice the molecules \( R'' R_{2} SiO_{8} \) and
\( R_{2}SiO_{4} \) do not occur separated from one another, but occur intermingled
so that all the Si and O atoms appear to be equivalent. He points out
further that the formula of Tschermak agrees with none of the cubic
space groups. He comes to the conclusion that even the space group
\( O_{h}^{3} \) is inadequate as it does not fulfill all the requirements of the garnet
structure and only the space group \( O_{h}^{10} \) fits in exactly.
Further, these X-ray studies of garnets reveal that the \( R_2O_3 \) group as such does not exist in garnets and so the original general formula \( 3RO R_2O_3 3SiO_2 \) is incorrect. It is further shown that the linking of oxygen and silicon is not the same as indicated by the above formula, but is entirely different. This naturally throws doubt on the standard molecular ratio for garnets, viz., \( R_2O_3 SiO_2 \). (3 1 3) which results from such a formula. Though this ratio is valuable for all practical purposes and can be used for estimating the correctness of the chemical analyses, still it does not show the structural characteristics. Because, this ratio completely ignores the fact that most of the elements present in the garnet molecule are capable of replacing one another in the crystal lattice and that the \( R_2O_3 \) group as such is nonexistent.

In this connection, I would like to mention the work of Alderman\(^4\) who has analysed a garnet from Botallack, Cornwall which gives the following composition —

\[
\begin{align*}
\text{SiO}_2 & \quad 35.58, \quad \text{TiO}_2 \text{ trace, } \quad \text{Al}_2\text{O}_3 \quad 21.94, \quad \text{Fe}_2\text{O}_3 \text{ none, } \quad \text{FeO} \quad 38.54, \\
\text{MnO} & \quad 0.70, \quad \text{MgO} \quad 0.68, \quad \text{CaO} \quad 1.68, \quad \text{and } \quad \text{H}_2\text{O (below 105°)} \quad 0.12 \text{ per cent}
\end{align*}
\]

On recalculating the above analysis in terms of mineral molecules the following composition is obtained:

Almandite = 89.00, Spessartite = 1.65, Pyrope = 2.35, Grossularite = 4.51, Coundum = 1.79, Quartz = 0.06, Water = 0.12 per cent.

"Considering the garnet molecules alone and raising to a summation of 100, we have"

Almandite = 91.33, Spessartite = 1.69, Pyrope = 2.35 and Grossularite = 4.63 per cent. Alderman expresses this composition in a molecular formula \( (\text{Fe}^{3+}_{0.1}, \text{Mn}_{1.7}, \text{Mg}_{2.4}, \text{Ca}_{0.6})_{3} \text{Al}_{2} (\text{SiO}_4)_{3} \). This type of formula, though it is not correct, appears to be better suited to express the exact mineralogical composition of garnets than the various formulae proposed to the garnet group of minerals. It shows the mineral composition of the garnet without going outside the scope of the structural formula the atom numbers of which, as they do not show the exact mineralogical composition at first sight, are replaced by the percentage composition of the individual pure garnet which is represented by its characteristic divalent metal.
A serious defect with this type of formula is the representation of the trivalent metal. Of course it is easy when the trivalent metal is single, but it offers considerable difficulties in garnets where the trivalent group contains more than one metal. So this formula is applicable only to those garnets where the trivalent group contains only one metal. In garnets where this number is more than one, it is no use employing this formula as it complicates the whole problem.

Considering all these difficulties, it is better to use the generally accepted structural formula of the unit cell of the garnet as given by X-ray investigations.

The X-ray studies of garnets show that the unit cell of garnet contains 24 atoms of bivalent metals, 24 atoms of silicon, 16 atoms of trivalent metals and 96 atoms of oxygen. Thus the unit cell is exactly 8 times as big as the garnet molecule and so its formula can be expressed as follows:

\[ R''_2 R''_i Si_{24} O_{96} \]

Or better still more compactly as either 8 \( (R''_2 R''_i Si_{24} O_{96}) \) or \( 8[R' R'(SiO_4)] \).

The last one is perhaps the most satisfactory as it is in agreement with the original molecular formula for garnets as well as with the X-ray investigations showing the exact linkage of the silicon atoms in the unit cell of the garnet. The structural formula \( R''_2 R''_i Si_{24} O_{96} \) is here employed to examine some of the chemical analyses of garnets, in order to see whether they are in keeping with the results of X-ray investigations.

As the formula involves cumbersome calculations, it can be replaced by the empirical formula \( R''_2 R''_i Si_{24} O_{96} \), and the results obtained can be multiplied by 8 to fit in with the formula of the unit cell, viz.,

\[ 8(R''_2 R''_i Si_{12} O_{48}) \]

The empirical formula shows the composition of a single garnet molecule. Even though this garnet molecule as such is nonexistent according to the results of X-ray investigations, it is convenient to keep in such a molecule for purposes of calculation. The garnet molecule
contains therefore, 3 atoms of divalent metals, 2 atoms of trivalent metals, 3 atoms of silicon and 12 atoms of oxygen. These twelve atoms of oxygen per molecule form the largest ions and form the body work of the garnet structure. So this number of twelve oxygen atoms is of fundamental importance to the garnet structure and to the garnet molecule and therefore, it is of great chemical significance like the 24 atoms of oxygen to the tremolite structure. Various garnet analyses therefore can be discussed in terms of the number of atoms of each kind in the molecule. The number of atoms of each kind in all cases are calculated on a basis of 12 O. The results thus obtained are then tabulated as in table I, and the composition is represented according to the garnet structural formula.

Method of calculating the number of atoms of each kind:

The various oxides are first arranged, as shown in the following table, in the order of increasing effective radius of the respective metal ion in the first column and in the second the percentage by weight of the corresponding oxides are given. In the third column the numbers of oxide molecules obtained by dividing the percentage amount of oxide by its corresponding molecular weight are given. Then figures in column four are obtained by multiplying the number of molecules shown in column three with the number of oxygen atoms in the corresponding oxide molecule. Now all the figures in column four are added up and this sum divided into 12 gives the ratio by which the whole analysis is multiplied to put it on a basis of 12 O. With this in view column 3 is now multiplied by this ratio and also by the number of metal atoms in the corresponding oxide molecule and the results obtained are expressed in column 5. Thus column 5 shows the number of metal atoms of each kind on a basis of 12 O. Now the figures in column 5 are multiplied by 8 so that they can fit in with the formula R_{24}^{+} \text{R}_{10}^{+} \text{Si}_{24} \text{O}_{96} and the results are expressed in column 6. The ideal composition is given in column 7. Column 8 shows the atomic proportion. Let us now take into consideration a concrete case and work it up. Here in the following table a recent analysis of a garnet is employed for this purpose.
<table>
<thead>
<tr>
<th>Oxides</th>
<th>Per cent by weight</th>
<th>Number of molecules</th>
<th>Number of $O_2$ atoms</th>
<th>Number of metal atoms on a basis of 12 $O_2$</th>
<th>Number of metal atoms on a basis of 96 $O_2$</th>
<th>Ideal composition Oxygen 96</th>
<th>Atomic proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SiO_2$</td>
<td>79.10</td>
<td>0.6516</td>
<td>13032</td>
<td>$Si = 2.998$</td>
<td>$Si = 23.944$</td>
<td>$Si = 24$</td>
<td>$Si = 652$</td>
</tr>
<tr>
<td>$Al_2O_3$</td>
<td>19.61</td>
<td>0.1923</td>
<td>0.5769</td>
<td>$Al = 1.177$</td>
<td>$Al = 14.186$</td>
<td>$Al = 385$</td>
<td></td>
</tr>
<tr>
<td>$TiO_2$</td>
<td>0.24</td>
<td>0.0050</td>
<td>0.0060</td>
<td>$Ti = 0.0138$</td>
<td>$Ti = 0.1104$</td>
<td>$Al + Fe'' = 16$</td>
<td>$T_i = 3$</td>
</tr>
<tr>
<td>$Fe_2O_3$</td>
<td>3.73</td>
<td>0.0233</td>
<td>0.0699</td>
<td>$Fe'' = 0.2140$</td>
<td>$Fe'' = 1.712$</td>
<td>$T_i = 3$ $Al + Fe'' = 432$</td>
<td></td>
</tr>
<tr>
<td>$MgO$</td>
<td>0.19</td>
<td>0.0048</td>
<td>0.0048</td>
<td>$Mg = 0.0221$</td>
<td>$Mg = 0.1788$</td>
<td>$Al + Fe'' = 16$</td>
<td></td>
</tr>
<tr>
<td>$FeO$</td>
<td>1.71</td>
<td>0.0238</td>
<td>0.0238</td>
<td>$Fe'' = 0.8714$</td>
<td>$Fe'' = 0.8714$</td>
<td>$Fe'' = 47$</td>
<td></td>
</tr>
<tr>
<td>$MnO$</td>
<td>0.41</td>
<td>0.0056</td>
<td>0.0056</td>
<td>$Mn = 0.0257$</td>
<td>$Mn = 0.2056$</td>
<td>$Ca + Mg + Mn + Fe'' = 24$</td>
<td></td>
</tr>
<tr>
<td>$CaO$</td>
<td>34.85</td>
<td>0.6223</td>
<td>0.6223</td>
<td>$Ca = 2.859$</td>
<td>$Ca = 22.872$</td>
<td>$Ca + Fe'' + Mg$</td>
<td></td>
</tr>
</tbody>
</table>

Total = 26125

\[
\frac{12}{26125} = 0.00594
\]
From the table I, it can be gathered that this garnet shows an excess in the divalent metal group and a deficiency in the trivalent metal group and silicon.

The following tables show the values calculated on the same basis for the various analyses. Only 5 columns of figures are given, columns 3, 4 and 7 of the above table being dropped out, as they are not necessary. First of all one analysis of the Nellore garnets* is taken for consideration and it is not proposed to deal with the other analyses of Nellore garnets, as they are of specimens from which the included material is not removed. The TiO₂ content was not taken into consideration, as it was present as a separate titanium mineral.

Now the data given in table II (A) shows many interesting points for study. The number of metal atoms calculated on a basis of 96 O, though it includes fractions, approach very closely that of the garnet structural formula. The number of Si atoms corresponds exactly to that of the structural formula and so the excess of Al in this case is not accounted for. The most striking thing, however, is the deficiency shown by the divalent group of metals. So to make up this deficiency the excess Al and the ferrous iron are added on to the divalent metal group.

The interesting fact revealed by table II (B) is that the analysis not only shows an excess of Al, as it would have been considered as such previously, but also shows appreciable deficiency in the divalent metal group and silicon. Even after restoring this deficiency by the excess Al, it is found that still some excess Al is found which could not be accounted for.

Now let us take the analysis of Wagner quoted by Fermor in his recent paper on Kholarite", and see whether its composition shows the same relationship to the structural formula as the other garnets. The number of atoms of each kind is calculated from this analysis on the basis of 12 O and is shown in table II (C).

* "Proc Ind Acad Sci", Vol V, No 2, Sec A, 1937 (Author)
TABLE II (A)

Analysis Y*

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Per cent by weight</th>
<th>Number of metal atoms on the basis of 12 O</th>
<th>Number of metal atoms on the basis of 96 O</th>
<th>Atomic proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>38.40</td>
<td>Si=3 003</td>
<td>24 024</td>
<td>640</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>21.90</td>
<td>Al=2 016</td>
<td>16 128</td>
<td>429</td>
</tr>
<tr>
<td>FeO</td>
<td>0.22</td>
<td>Fe&quot;&quot;=0.014</td>
<td>0.112</td>
<td>3</td>
</tr>
<tr>
<td>MgO</td>
<td>4.60</td>
<td>Mg=0.5400</td>
<td>4.120</td>
<td>115</td>
</tr>
<tr>
<td>FeO</td>
<td>27.84</td>
<td>Fe&quot;&quot;=1.816</td>
<td>14.528</td>
<td>387</td>
</tr>
<tr>
<td>MnO</td>
<td>0.26</td>
<td>Mn=0.017</td>
<td>0.126</td>
<td>4</td>
</tr>
<tr>
<td>CaO</td>
<td>6.89</td>
<td>Ca=0.5770</td>
<td>4.620</td>
<td>12.5</td>
</tr>
</tbody>
</table>

* Analysis of a Nellon granite (Author)
Table II (B)

*The Botallack garnet analysed by Alderman*

(Alderman has also calculated from this analysis the number of atoms of each kind on the basis of \(12\ O\) and has reduced them to the fundamental ratio \(3\ 2\ 3\).)

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Per cent by weight</th>
<th>Number of metal atoms on the basis of (12\ O)</th>
<th>Number of metal atoms on the basis of (96\ O)</th>
<th>Atomic proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SiO}_2)</td>
<td>33.58</td>
<td>2.936</td>
<td>23.488</td>
<td>({\begin{align*} \text{Si}=23.488\end{align*})</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
<td>21.94</td>
<td>2.172</td>
<td>17.376</td>
<td>(\begin{align*} \text{Al}=16344\end{align*})</td>
</tr>
<tr>
<td>(\text{MgO})</td>
<td>0.68</td>
<td>0.084</td>
<td>0.672</td>
<td>(0.520)</td>
</tr>
<tr>
<td>(\text{FeO})</td>
<td>38.34</td>
<td>2.658</td>
<td>21.224</td>
<td>(23480)</td>
</tr>
<tr>
<td>(\text{MnO})</td>
<td>0.70</td>
<td>0.049</td>
<td>0.392</td>
<td>(=24)</td>
</tr>
<tr>
<td>(\text{CaO})</td>
<td>1.68</td>
<td>0.149</td>
<td>1.192</td>
<td>(=80)</td>
</tr>
</tbody>
</table>

\[\text{Al}=16344 \div 520 = 31.23\]
<table>
<thead>
<tr>
<th>Oxides</th>
<th>Per cent by weight</th>
<th>Number of metal atoms on the basis of 12 O</th>
<th>Number of metal atoms on the basis of 96 O</th>
<th>Atomic proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>40.79</td>
<td>3,052</td>
<td>24,416</td>
<td>680</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.81</td>
<td>1,128</td>
<td>9,024</td>
<td>125.6 × 2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>14.35</td>
<td>0.8054</td>
<td>6,418</td>
<td>89.7 × 2</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>1.03</td>
<td>0.60</td>
<td>0.480</td>
<td>6.7 × 2</td>
</tr>
<tr>
<td>MgO</td>
<td>17.89</td>
<td>2,004</td>
<td>16,032</td>
<td>447</td>
</tr>
<tr>
<td>FeO</td>
<td>7.39</td>
<td>0.461</td>
<td>3,688</td>
<td>23,220</td>
</tr>
<tr>
<td>CaO</td>
<td>5.46</td>
<td>0.4875</td>
<td>3,500</td>
<td>98</td>
</tr>
</tbody>
</table>

This same analysis when calculated into garnet molecules by Fermor gave an excess of 1.17 per cent of Fe₃O₄ while the above table shows a slightly lower value for the trivalent metal group. The divalent group of metals also show an appreciable deficiency and further this deficiency cannot be made up as the trivalent group itself shows no excess. The excess value shown by Si is perhaps due to quartz.

Now an analysis of a garnet from the garnet mines, Sarwar, Kishengarh State (Rajputana) (J.371), given by Fermor is taken for consideration as it shows some resemblance to the Nellore garnets.
It can be gathered from the above table that this analysis shows a general deficiency in all the three groups, the whole of the ferric iron shown by the analysis being taken into the divalent group of metals. But when these results are calculated into garnet molecules, according to Fermor, they give a surplus of 0.26 per cent of $\text{Al}_2\text{O}_3$ and 1.30 per cent of $\text{Fe}_2\text{O}_3$. The microscopic examination, however, did not reveal the presence of ferric oxide.

This garnet is peculiar in one respect that its microscopic properties are not supported by the chemical composition either when it is calculated in mineral molecules or when it is calculated as the number of metal atoms on the basis of 96 $O$. This will become apparent when the observed microscopic properties are compared with the calculated values. Fermor gives the microscopic characters as follows —

"J 371 —

Under the microscope this garnet is practically colourless, and shows numerous inclusions of three sorts. The most abundant are
minute needles arranged in several parallel sets, oriented presumably with some reference to the crystallographic habit of the mineral, but as the specimen sectioned showed no crystal faces this relationship is not obvious. The refractive index of these needles is greater than that of garnet, the polarization tints range up to blue of the first order, the extinction is oblique, ranging from 15° up to 39° with reference to the long axis of the needles, the ray nearest the vertical axis being sometimes that of lesser and sometimes that of greater elasticity. The colour of these needles is very pale yellowish. The second kind of inclusions is in broader needles, polarizing in first order grey. There are also a few grains of a mineral of a lower refractive index than the garnet and very low birefringence, and probably apatite. The above list of inclusions sounds formidable, but the total amount is exceedingly small.

From the above microscopic evidence it appears that the accicular inclusions met with in this garnet are probably of sphene or kyanite. But, the presence of titanium is not indicated in the chemical analysis, and it is not known whether the presence of titanium was tested for. It is difficult to take it as kyanite (Al₂O₃-SiO₂) as the atomic calculation on the basis of 96 O shows that both Si and Al are deficient. But this deficiency is not borne out either by the ratio of atomic proportions, which is 2.98 2.305 (RO R₂O₃ SiO₂) or by the ratio of molecular proportions, which is 2.98 1.305 in these garnets.

Now we shall take into consideration another analysis which shows deviations from the normal ratio R O. This analysis is of an almandite from Dillenberg, given by Gossmer, and is calculated as shown in the following table into number of metal atoms on the basis of 96 O.

Column 5 (a) shows the atomic ratio of this garnet assuming that all the ferric iron shown by the analysis is due to the oxidation of the original ferrous iron and 5 (b) shows the ratio assuming that all the ferric iron is present in such the garnet.

As these calculations almost always involved fractional results to be applied to the indivisible atom numbers, it is reasonable to postulate that it is not due to experimental error but is due perhaps to some
<table>
<thead>
<tr>
<th>Oxides</th>
<th>Per cent by weight</th>
<th>Number of metal atoms on the basis of 12 O</th>
<th>Number of metal atoms on the basis of 96 O</th>
<th>Atomic proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td>SiO₂</td>
<td>27 00</td>
<td>3 007</td>
<td>24 056</td>
<td>617 3.085</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20 36</td>
<td>1 947</td>
<td>15 576</td>
<td>400 2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2 09</td>
<td>0 1274</td>
<td>1 019</td>
<td>26 15.607</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>1 52</td>
<td>0 1852</td>
<td>1 482</td>
<td>76 654</td>
</tr>
<tr>
<td>FeO</td>
<td>30 80</td>
<td>2 088</td>
<td>16 688</td>
<td>428 3.27</td>
</tr>
<tr>
<td>MnO</td>
<td>7 57</td>
<td>0 5199</td>
<td>4 159</td>
<td>428 628</td>
</tr>
<tr>
<td>CaO</td>
<td>0 98</td>
<td>0 08533</td>
<td>0 683</td>
<td>17 628</td>
</tr>
</tbody>
</table>

|        |                    |                                          |                                          |                   |
|        |                    |                                          |                                          | (b)               |
|        |                    |                                          |                                          |                   |
|        |                    |                                          |                                          |                   |
|        |                    |                                          |                                          | 2 897             |
|        |                    |                                          |                                          | 2 948             |
structural phenomenon as suggested by Fermor—"The extent to which the percentage proportions of the garnet 'molecules' cannot be adjusted to integral fractions of 24 for the divalent atoms and of 16 for the trivalent atoms must be regarded, in so far as it is not due to experimental error, as a measure of slight variation from the composition of one unit cell of garnet to another in the same specimen."

Recently it was discovered by X-ray studies of garnets that the miscibility gaps between almandite and grossularite, almandite and andradite, andradite and pyrope, pyrope and grossularite cannot be explained directly by the structural properties of garnet, because there is no feature in the structure of garnets to warrant the assumption of limited miscibility amongst the various members of the garnet group. This reasoning is aptly presented by Fermor in his recent paper on *Khohanite*, a new garnet, to point out that the miscibility gap between almandite and andradite-grossularite cannot be explained by structural values. He quotes many analyses which fall in the miscibility gap of Boeke’s diagram, to show that the theory that miscibility gaps have a chemical or structural significance is not tenable. Fermor’s reasoning is that, as the atomic structure does not offer any structural reason for the limited miscibility in garnets, this limited miscibility is perhaps controlled mainly by the mode of origin of the garnet. In view of the various data collected from literature, I should think that this appears to be the best view of the matter. As different crystals from the same hand specimen of rock show difference in composition, it has to be assumed that the composition of the garnet is controlled by the mode of origin of the individual crystal which again is dependent on the composition of the parent rock mass and also the way in which the various elements were concentrated in the parent rock just before the crystallisation of garnet. Ford also expresses a similar opinion. "The question naturally arises in this connection, whether this limited miscibility of the different garnet molecules depends upon inherent characteristics of the garnet group and that in a certain case only a definite amount of one molecule can combine with one another, or whether it is brought about by natural restrictions of the ordinary mode of occurrence of that garnet. In other words, this limited miscibility
may not depend upon chemical restrictions, but rather upon restrictions, imposed by the conditions of the origin of the garnets.''

Thus it can now be concluded that the miscibility gaps present in the garnet group of minerals is merely accidental and is mainly brought about by the particular mode of origin of the garnets and the chemical composition of the parent rock mass, that is, the amount and distribution of available elements present in the original rock. It is perhaps due to variations in the usual mode of origin that the composition of many garnet crystals fall exactly in the statistically established miscibility gaps. Such garnets, though rare, are not peculiar. They are as natural as any other garnet.

SUMMARY

1. X-ray investigations on the garnet structure by Menzci and Hensch are reviewed with a view to apply them to some of the analyses of garnets and to the garnet formula in general.

2. The formula proposed by Alderman to the specimens of garnet from Botallack, Cornwall, is critically examined.

3. Considering various difficulties, it is found that it is better to use the generally accepted structural formula of the unit cell of garnet as given by X-ray investigations. The inadequacy of the standard molecular ratio \( R^9O_7, R^9_5SiO_4 \) to explain the various intricate problems connected with the mineralogical study of garnets is pointed out.

4. The structural formula \( R^9_{21}, R^9_{10}Si_2, O_{96} \) is employed to examine some of the chemical analyses of garnets in order to see whether they are in keeping with the results of X-ray investigations. For this purpose the various analyses are calculated into number of atoms of each kind on a basis of 12 \( O \) or 96 \( O \).

5. The method employed to calculate the number of atoms of each kind is illustrated by a table. The following analyses were taken for this critical examination —

(a) Analysis of one of the purified Nellore garnets (the author) (Y)

(b) Analysis of the Botallack garnet (Alderman)
(c) Analysis of Wagner quoted by Fermor in his recent paper on Khoharite

(d) Analysis of a garnet from the garnet mines, Sarwar, Kishengarh State, Rajputana (J 371 given in one of the papers of Fermor)

(e) Analysis of an Almandite from Dillenberg given by Gossner

6 The miscibility gaps present in the garnet group of minerals remains unexplained except on the view that they are due to the particular mode of origin of the garnets, and the chemical composition of the surrounding rock mass during the formation of the garnet.

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