Rings, topology, and the density of tectosilicates

LARS STIXRUGE, M.S.T. BUKOWINSKI
Department of Geology and Geophysics, University of California at Berkeley, Berkeley, California 94720, U.S.A.

ABSTRACT

A review of density data for tectosilicates shows that variations in density within a single framework type are typically an order of magnitude smaller than the twofold variations among different framework types. To help explain this large range of densities, we have analyzed the geometric and topologic properties of different frameworks. We used the geometry and statistics of clusters to construct a predictive model for the framework density of tectosilicates. Ring statistics and geometries, together with a simple theory of the effects of ring formation on framework density, lead to the definition of a framework-specific characteristic ring size. We show that this characteristic ring size increases with increasing framework density.

INTRODUCTION

Tectosilicates, including the ubiquitous silica polymorphs and feldspars as well as feldspathoids, scapolites, and the technologically important zeolites, are the most abundant minerals in the Earth's crust (see, e.g., Hurlbut and Klein, 1977). Although the few hundred distinct species vary widely in color, habit, composition, and other physical properties, we focus here on how variations in density are controlled by differences in the underlying framework structure, the continuous three-dimensional network of corner-sharing SiO$_4$ and AlO$_4$ tetrahedra common to all tectosilicates. In addition to its fundamental crystallographic significance, the relationship between density and framework structure is central to the design and synthesis of low-density zeolites important to industry (Smith and Dytynch, 1984; Davis et al., 1988; Brunner and Meier, 1989) and may also elucidate the relation between the highly variable framework structures and compression of silicate liquids (Stixrude and Bukowinski, 1989).

Although the total number of tectosilicate species is large, many have topologically identical frameworks, and only about 80 distinct underlying framework structures have been observed in naturally occurring and synthetic specimens (Meier and Olson, 1988; Smith, 1977, 1978, 1979; Smith and Bennett, 1981, 1984). The variation in density among different types of frameworks is much larger than variations within a single framework type. For example, the differences in molar volume among the myriad feldspar species are more than an order of magnitude smaller than the difference between the molar volume of the densest known framework, coesite, and that of the sparsest, faujaisite, which differ in density by a factor of two, whereas other theoretically proposed structures are less dense by a factor of three than coesite (Meier, 1986). The goal of this paper is a description of the geometry and topology of framework structures that can explain this remarkable variation in density.

The fact that local geometries (as measured by (Si,Al)-O and (Si,Al)-(Si,Al) distances and coordination numbers) in different framework structures are nearly identical makes the wide range of observed densities even more remarkable. This has led several authors to examine the relationship between density and topological elements of frameworks such as clusters and rings. For instance, a correlation between cluster populations and density has been observed (Brunner, 1979; Akporiaye and Price, 1989) and a relationship between the smallest ring in a framework and its density has recently been noted (Liebau, 1988; Brunner and Meier, 1989).

Here we combine topologic and geometric measures of clusters and rings to examine more closely their relationship to density. We first review the concept of framework density and describe in some detail its wide variability among tectosilicates. We then describe the notion of a cluster and present a simple predictive model that relates the topology and geometry of clusters to framework density. Finally, we critically examine the definition of a ring and introduce a theory for the effect of ring formation on cluster size and, thus, framework density.

Frameworks and framework density

Framework density (FD), used by many previous authors in studies of tectosilicates (e.g., Brunner and Meier, 1989), is defined as the number of tetrahedrally coordinated atoms, or T atoms (usually Si or Al), per unit volume. This is a convenient measure, since it allows us to directly compare tectosilicates with different chemical compositions. The wide range of FD for the framework types considered in this study is shown in Table 1. Although many species may share a single framework type, the variability of FD within a single framework type is much less than the total variability in FD. For example,
TABLE 1. Tectosilicate framework densities

<table>
<thead>
<tr>
<th>Framework</th>
<th>FD</th>
<th>L</th>
<th>FD*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gmelinite</td>
<td>14.59</td>
<td>3.131</td>
<td>15.04</td>
<td>Fischer (1968)</td>
</tr>
<tr>
<td>Chabazite</td>
<td>14.47</td>
<td>3.141</td>
<td>15.06</td>
<td>Calligaris et al. (1982)</td>
</tr>
<tr>
<td>ZK</td>
<td>14.68</td>
<td>3.128</td>
<td>15.09</td>
<td>Meier and Kokotallo (1965)</td>
</tr>
<tr>
<td>Offretite</td>
<td>15.52</td>
<td>3.131</td>
<td>16.00</td>
<td>Gard and Tait (1972)</td>
</tr>
<tr>
<td>Erionite</td>
<td>15.64</td>
<td>3.136</td>
<td>16.19</td>
<td>Staples and Gard (1959)</td>
</tr>
<tr>
<td>Levene</td>
<td>15.23</td>
<td>3.177</td>
<td>16.39</td>
<td>Merlino et al. (1975)</td>
</tr>
<tr>
<td>Philipsite</td>
<td>15.82</td>
<td>3.144</td>
<td>16.50</td>
<td>Rinaldi et al. (1974)</td>
</tr>
<tr>
<td>Gismondine</td>
<td>15.29</td>
<td>3.197</td>
<td>16.77</td>
<td>Fischer (1963)</td>
</tr>
<tr>
<td>Heulandite</td>
<td>17.12</td>
<td>3.115</td>
<td>17.36</td>
<td>Alberti and Vezzalini (1983)</td>
</tr>
<tr>
<td>Laumontite</td>
<td>17.78</td>
<td>3.084</td>
<td>17.51</td>
<td>Bartl and Fischer (1967)</td>
</tr>
<tr>
<td>Mordenite</td>
<td>17.03</td>
<td>3.130</td>
<td>17.53</td>
<td>Meier (1961)</td>
</tr>
<tr>
<td>Losod</td>
<td>15.78</td>
<td>3.221</td>
<td>17.70</td>
<td>Sieber and Meier (1974)</td>
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<tr>
<td>Sodalite</td>
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<td>3.136</td>
<td>17.81</td>
<td>Lons and Schulz (1967)</td>
</tr>
<tr>
<td>Cancrinite</td>
<td>16.58</td>
<td>3.179</td>
<td>17.87</td>
<td>Jarchow (1965)</td>
</tr>
<tr>
<td>Natroline</td>
<td>17.73</td>
<td>3.111</td>
<td>17.92</td>
<td>Pechar et al. (1983)</td>
</tr>
<tr>
<td>Dachiardite</td>
<td>17.34</td>
<td>3.148</td>
<td>18.16</td>
<td>Gottiardi and Meier (1963)</td>
</tr>
<tr>
<td>Epistilbite</td>
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<td>3.133</td>
<td>18.22</td>
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<td>Rohman et al. (1965)</td>
</tr>
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<td>ZSM-23</td>
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<td>Rohman et al. (1965)</td>
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<tr>
<td>ZSM-48</td>
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<td>3.091</td>
<td>19.75</td>
<td>Schlenker et al. (1985)</td>
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<td>Biklitite</td>
<td>20.29</td>
<td>3.100</td>
<td>20.29</td>
<td>Kocman et al. (1974)</td>
</tr>
<tr>
<td>Feldspar</td>
<td>22.25</td>
<td>3.096</td>
<td>22.16</td>
<td>Colville and Ribbe (1968)</td>
</tr>
<tr>
<td>CaGao3</td>
<td>21.49</td>
<td>3.131</td>
<td>22.14</td>
<td>Delsolero and Muller-Buschbaum (1973)</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>23.28</td>
<td>3.074</td>
<td>22.70</td>
<td>Peacor (1973)</td>
</tr>
<tr>
<td>CaAl2Si2O8</td>
<td>23.38</td>
<td>3.075</td>
<td>22.80</td>
<td>Takuchi et al. (1973)</td>
</tr>
<tr>
<td>Marialite</td>
<td>21.75</td>
<td>3.141</td>
<td>22.63</td>
<td>Levien and Papke (1976)</td>
</tr>
<tr>
<td>Banasilite</td>
<td>22.52</td>
<td>3.128</td>
<td>23.14</td>
<td>Hagai (1973)</td>
</tr>
<tr>
<td>Cordierite</td>
<td>23.15</td>
<td>3.146</td>
<td>24.20</td>
<td>Cohen et al. (1977)</td>
</tr>
<tr>
<td>Quartz</td>
<td>28.52</td>
<td>3.057</td>
<td>25.43</td>
<td>Levien et al. (1980)</td>
</tr>
<tr>
<td>Coesite</td>
<td>29.28</td>
<td>3.086</td>
<td>26.87</td>
<td>Gie:minger et al. (1987)</td>
</tr>
</tbody>
</table>

Note: The mineral chosen to represent each framework type is listed along with the reference to its structure. For alternative species see compilations by Meier and Olson (1988), Smith (1977, 1978, 1979), and Smith and Bennett (1981, 1984). L is the average T-T distance. Units of FD and FD* are nm^-3 and L is in angstroms. FD* is defined by FD* = FD(L/L$_0$), where the standard T-T distance L$_0$ is chosen to be 3.1 Å.

it has long been recognized that the FD of feldspars varies inversely with the ionic radius of the interstitial cation (see the review by Smith and Brown, 1988). However, Figure 1 shows that this variation, along with changes in FD due to differences in Al-Si ordering and relative concentration, is less than 12% compared with the twofold total variability among different framework types. Thus, a description of the geometric and topological variations among different framework types on which FD depends most strongly is central to an understanding of the densities of tectosilicates.

The measure of framework density suggests a simplified conceptual picture of tectosilicate structure that will be useful in characterizing different framework types (see also Smith, 1982, p. 161ff). Since framework density depends only on the number of T atoms, we form the simplified structure by removing all O atoms and interstitial cations from the structure. Then, since in the actual structure each T atom is bonded to four O atoms, each of which in turn is bonded to one other T atom, we think of T atoms that share a common O as being linked to one another in the simplified structure. The relationship between simplified and actual structures is illustrated schematically in Figure 2. Since all of the properties considered here, including framework density and measures of cluster and ring size, are identical in both the simplified and actual structures, the two structural representations are completely equivalent for the purposes of this paper.

This conceptual picture of tectosilicate structure can be used to examine the relationship between framework density and measures of local geometry, such as bond length and coordination number. In many crystal structures, variations in these quantities can be related directly to variations in density. For example, the densities of many materials with simple structures, such as metals, can be characterized entirely by a packing fraction of atoms that depends mostly on interatomic distance and coordination number (e.g., Kittel, 1976). These concepts can sometimes be fruitfully applied to silicates: the difference in density between quartz and stishovite can be attributed to the increase from tetrahedral to octahedral coordination (Stishov and Popova, 1961) and the in...
crease with pressure in the density of quartz can be attributed to a decrease in T-T distance (Stixrude and Bukowinski, 1988, 1989). However, the variability of local geometries among different framework types is insufficient to explain the observed variability of FD among tectosilicates. Applying our simplified conceptual picture of tectosilicate structure, we see that each T atom is always linked to four other T atoms, and thus all framework structures are fourfold coordinated. Further, the variations in T-T distance, although inversely related to FD, are insufficient to explain the total variability of FD. This is illustrated in Figure 3, which shows the wide variability of framework density among tectosilicates and the inability of variations in T-T distance (L) to account for this variability.

As an illustrative example, the number of Qth linked neighbors for a cluster in a Bethe lattice (Bethe, 1935; Domb, 1960) with a coordination number of four (Fig. 4) is given by

$$N_Q = 4 \times 3^{Q-1}$$

and the total number of T atoms in such a cluster of size Q is given by:

$$M_Q = 1 + 4 \times \sum_{i=0}^{Q-1} 3^i = 2 \times 3^Q - 1.$$ (3)

This particularly simple framework, sometimes referred to as a tree, will prove useful when we discuss rings below. In addition to $N_Q$ and $M_Q$, we have computed $D_Q$, the average distance to the Qth linked neighbor shell for each of the framework structures considered in this study up to $Q = 6$. Some of the results of these computations, discussed in detail in Appendix 1, are listed in Tables 2 and 3.

In order to relate clusters to tectosilicate density, we construct a simple model that allows the calculation of framework density from the number of T atoms in a cluster ($N_Q$ and $M_Q$) and the spatial dimensions of the cluster ($D_Q$). In this model, we consider a framework to be composed of many clusters of a given size Q. Although one may divide the framework into clusters in such a way that the overlap among clusters is minimized, in general, adjacent clusters will share some number of T atoms. We assume that only the outermost T atoms, those in the Qth linked neighbor shell, are shared and that each of
these \( N_Q \) atoms is shared on average between two clusters. If we also approximate the shape of each cluster as a sphere, the calculated framework density for our model is

\[
FD = \frac{(M_{Q-1} + \frac{1}{2}N_Q)}{V(D_Q)}
\]

where

\[
V(D_Q) = 4\pi D_Q^3/3.
\]

In order to assess the validity of this simple model, we compare FD calculated from Equation 4, using \( Q = 6 \), to the actual FD for all the framework structures listed in Table 1. Figure 5 shows the excellent agreement between Equation 4 and actual framework densities: the root-mean-square deviation between model and data is 3.0%. For much larger \( Q \), the approximation that only atoms in the \( Q \)th shell are shared will become less accurate, whereas for a much smaller \( Q \), different frameworks become indistinct: in the limit of \( Q \to 1 \), all frameworks have \( N_Q = 4 \). Nevertheless, the calculated FD values are insensitive to small changes in \( Q \): for \( Q = 5 \), the root-mean-square deviation between calculated and actual FD is 4%. Thus, although the assumptions upon which the model is based can only be approximately correct, the model is remarkably accurate in predicting actual framework densities from the properties of microscopic clusters of \( T \) atoms, suggesting a close association between the structure of clusters and that of the entire framework.

Further examination of the properties of clusters shows that the variability of topological measures (\( M_{Q,N} \)), rather than geometric measures (\( D_Q \)), of cluster size are primarily responsible for the observed variation in framework density. There is, for example, a good correlation between the actual FD for all the framework structures listed in Table 4 and discussion of rings below. For much larger \( Q \), the approximation that only atoms in the \( Q \)th shell are shared will become less accurate, whereas for a much smaller \( Q \) different frameworks become indistinct: in the limit of \( Q \to 1 \), all frameworks have \( N_Q = 4 \). Nevertheless, the calculated FD values are insensitive to small changes in \( Q \): for \( Q = 5 \), the root-mean-square deviation between calculated and actual FD is 4%. Thus, although the assumptions upon which the model is based can only be approximately correct, the model is remarkably accurate in predicting actual framework densities from the properties of microscopic clusters of \( T \) atoms, suggesting a close association between the structure of clusters and that of the entire framework.

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### RINGS

Although a lucid discussion of the possibility for wide structural variation in tetrahedral frameworks appeared as early as 1932 in Zachariasen's pioneering work on glasses, the systematic description of the topology of different framework types is more recent, apparently originating with Bernal's (1964) suggestion that rings, rather
In the most general sense, a ring may be taken as any return path in the framework. However, this is not a very useful definition since there is an infinite number of such rings, and the number of rings of a given size increases without limit with the size of the ring. Thus for practical and aesthetic reasons, identification of a small set of rings as being somehow fundamental is desirable. The older definition, first given by King (1967), counted the set of six smallest rings, one through each of the six pairs of T-T links emanating from a T atom, as fundamental. This definition, however, leads to ambiguities in ring counting (Smith, 1978) and ignores the common occurrence of more than one ring of the same size passing through a single pair of T-T links (Belch and Rice, 1987). On a practical level, many different framework structures

than the coordination numbers so profitably employed in describing ionic and metallic materials, should be the primary topological measure of covalently bonded structures. Thus, the characterization of physical models of silica glass built shortly thereafter (Evans and King, 1966; Bell and Dean, 1966) included the first complete measurements of the ring statistics of a tectosilicate structure (King, 1967). However, the definition of a ring used in these early papers, very similar to that used by Smith (1977, 1978, 1979) and Smith and Bennett (1981, 1984) in their more recent work on the derivation of crystalline tectosilicate structures, differs from the one used in the present study; a detailed discussion of the definition of a ring is therefore required.

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have identical ring statistics by this definition (Smith, 1977), suggesting that a new definition would be useful. We find the simplest and most appealing definition of a fundamental ring, introduced by Marians and Hobbs (1989b), to be any ring that cannot be divided into two smaller ones. It is free of the ambiguities of the older definition and results in a much greater variability of ring statistics among different framework structures. Some of the differences between this and the older definition of fundamental rings are illustrated schematically in Figure 8.

We used this new definition of a fundamental ring and an algorithm described in Appendix 1 to determine the ring statistics for all the framework structures examined in this study (see Table 4). These are the first measurements of ring statistics of tectosilicates, other than the silica polymorphs (Marians and Hobbs, 1989b), that are based on the new definition.

To analyze the ring statistics of tectosilicates, we introduce a simple theory of the effects of ring formation on framework density. We shall argue that, in general, ring formation tends to decrease framework density, and that forming a small ring affects the density much more than forming a larger one. To illustrate this we will consider only clusters, rather than entire frameworks, and assume that ring formation affects only cluster topology \( (M_0, N_0) \) and not geometry \( (D_0) \). These limitations are justified, since we have shown that cluster topology is closely related to framework density (Fig. 5) and that cluster geometries of frameworks with widely varying ring statistics are very similar (Fig. 7). Further, we make the simplifying assumption that the relative effect of different sizes of rings is the same for all frameworks. This allows us to base our discussion on a simple framework, the Bethe lattice described earlier, which will yield an analytic expression for the effect of ring formation on framework density.

Figure 9 shows the effect of ring formation for different sizes of rings on the cluster topology of the Bethe lattice. For example, the formation of a three-membered ring belonging to the central T atom means that two first neighbors of the central T atom become linked to each other. However, because of the restriction that every T atom can be linked to only four others, these two first neighbors must now break their links with T atoms in the second neighbor shell of the central T atom, thus pruning from the tree two branches radiating outward from two T atoms in the second neighbor shell. Similarly, forming a four-membered ring belonging to the central T atom means that two T atoms in the second neighbor shell must coalesce into one. Again, the restriction of four-coordination then requires that four branches be pruned beginning in the third neighbor shell. More generally, for
### Table 4. Ring statistics

<table>
<thead>
<tr>
<th>Framework</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>K*</th>
</tr>
</thead>
<tbody>
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Note: The average number of rings of size $K$ passing through a single T atom averaged over all T atoms in the structure is given by $f(K)$. (Characteristic ring size defined by Equation 11).

A plot of $P^*(K)$ (Fig. 9) shows it to be rapidly decreasing function of ring size, emphasizing the greater effect of small rings on framework density.

Our theory predicts that a measure of ring size that takes into account the greater role played by small rings will increase with increasing framework density. Thus, we define a characteristic ring size:

$$K^* = \sum K f(K) W(K) / \sum f(K) W(K),$$

where the sum are over $K$, $f(K)$ is the number of $K$ rings in a structure (Table 4) and $W(K)$ is a weighting function which is a decreasing function of $K$. If, as the theory suggests, we identify $W(K)$ with $P^*(K)$, we find a significant positive correlation between $K^*$ and framework density (Fig. 10). We attribute this result to the greater pruning efficiency of small rings compared with large ones. Thus, despite the simplifications built into our theory, it serves to elucidate the close relationship between ring statistics and framework density.

For odd-membered rings:

$$P^*(K) = 2/3^{(K-2)},$$

and for even-membered rings:

$$P^*(K) = 1/3^{(K-3)}.$$
Our observation that characteristic ring size increases with framework density is fully consistent with previous observations, including the recent work of Liebau (1988) and Brunner and Meier (1989), noting a systematic trend toward lower observed framework density with decreasing size of the smallest ring in the framework. Connections between the existence of small rings in a network and small values of \( N_n \) have also been noted (Brunner, 1979; Akporiaye and Price, 1989), again fully consistent with our results.

The perhaps counterintuitive relationship between ring size and framework density is topological in nature, via the pruning mechanism, and is not attributable to any greater propensity for large rings to crumple or fold up compared with small rings, as has been suggested (Marjans and Hobbs, 1989b). In fact, rings with larger topological size (\( K \)) are also geometrically larger. By measuring the geometry of rings in tectosilicates, we show that plausible measures of the effective density of a ring decrease with increasing ring size \( K \). We define an effective...
density of a ring:

\[ \rho(K) = \frac{K}{R_0^2} \]

where \( R_0 \) is the radius of gyration (root-mean-square distance from the center of mass):

\[ R_0^2 = \frac{1}{2} \sum_{i<j} r_{ij}^2 \]

where \( r_{ij} \) is the distance between \( i \) atoms for an effective dimensionality of a ring, which may be thought of as lying between two and three, since rings are nearly planar structures. We have determined \( R_0 \) for all rings of this study and compared these values to the value of \( R_0 \) for planar rings:

\[ R_0 (\text{Planar}) = \frac{1}{2} L \csc(\pi/K) \]

where \( L \) is the T-T distance, and to variations in \( R_0 \) for constant effective ring density:

\[ R_0 [\rho(K) = \text{constant}] \propto K^{1/4} \]

Figure 11 shows that, although rings deviate systematically from planarity with increasing ring size, the fact that \( R_0 \) increases much more rapidly than Equation 15 for \( d = 2 \) or \( d = 3 \) means that any plausible measure of effective ring density will decrease with increasing ring size. Thus, rings crumple only slightly, and one should not think of increasing characteristic ring size with increasing density as being accommodated by the crumpling of rings. This indicates that the density of rings, which are two-coordinated, nearly two-dimensional structures, cannot be simply related to the density of three-dimensional four-coordinated frameworks.

**Summary**

We have examined in detail the density of tectosilicates, minerals based on frameworks with identical coordination numbers and nearly identical bond lengths yet vastly different densities. We have shown how topological elements of frameworks, such as clusters, can be used to form predictive models of framework density. We described the advantages of a new definition of rings and presented the first measurements of ring statistics of tectosilicates, other than the silica polymorphs, based on this definition. Finally, we have described a simple theory that relates ring formation to framework density and used this to define a characteristic ring size that shows a strong positive correlation with framework density. The counterintuitive increase in ring size with increasing density is attributed to a topological pruning mechanism and is not related to deformation of rings. Although the picture relating ring statistics to framework density presented here is simple and can be refined, it provides a basis for rationalizing the densities of tectosilicates. It provides further support for the importance of structures containing four- and three-membered rings in the search for new low-density zeolites. Finally, it is sufficiently general to provide a first-order description of the complex changes in silicate-liquid framework structure caused by increasing pressure (Stixrude and Bukowinski, 1990).

**Acknowledgments**

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MANUSCRIPT ACCEPTED AUGUST 10, 1990
APPENDIX 1. MEASUREMENT OF CLUSTER AND RING STATISTICS

The description of the algorithm for finding cluster parameters, \( N_c \) and \( M_c \), and ring statistics, \( R(k) \), is presented in a way that allows the results to be easily reproduced by hand, at least for a small \( Q \). For \( Q \) larger than three or four, the logical operations are too numerous. We used a computer program to generate all the results of this paper. Throughout, the quartz structure is used as an example, since it contains the smallest number of \( T \) atoms per unit cell.

The first step is to identify each atom in the structure with a four-part label: \( (i,j,k,l) \), where \( i \) uniquely identifies all the atoms in the unit cell and \( j,k,l \) define a lattice translation vector in the basis defined by the lattice vectors \( a,b,c \) (i.e., \( t = ia + ja + kc \), where \( t \) is a translation vector). \( T-T \) links are then identified by searching for all \( T \) atoms that lie within a certain distance of each \( T \) atom in the unit cell (3.5 Å is an appropriate cutoff for all the structures in this study). The result is a linkage table that contains all linkage information for the entire structure. That is, if we know that \( (1,0,0,0) \) is linked to \( (2,1,0,1) \), then \( (1,0+j',0+k',0+l') \) is linked to \( (2,1+j',0+k',1+l') \) for all \( j',k',l' \).

As an example, if we identify the atoms in the unit cell of quartz in the following way:

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then the resulting linkage table is

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<td>(2,0,-1,-1), (2,1,0,-1), (3,0,-1,0), (3,0,0,0)</td>
</tr>
<tr>
<td>(2,0,0,0)</td>
<td>(1,-1,0,1), (1,0,1,1), (3,-1,0,0), (3,0,0,0)</td>
</tr>
<tr>
<td>(3,0,0,0)</td>
<td>(1,0,0,0), (1,0,1,0), (2,0,0,0), (2,1,0,0).</td>
</tr>
</tbody>
</table>

Because the linkage table establishes the linkage for the entire structure, all subsequent operations involved in finding cluster and ring statistics involve only the linkage table, and no further reference to atomic coordinates is made.

The cluster up to \( Q = 3 \) of atom \((1,0,0,0)\) in quartz is shown in Figure 1A. The first neighbor shell is obtained directly from the linkage table, whereas the second neighbor shell is constructed by finding the linked neighbors of the atoms in the first linked neighbor shell and so on for larger \( Q \). For instance, the linkage table tells us that the first linked neighbors of atom \((2,0,0,0)\) are \((1,-1,0,1), (1,0,1,1), (3,-1,0,0), (3,0,0,0)\). Once the cluster is constructed, the number of distinct neighbors in each neighbor shell are counted to give \( N_c \) and \( M_c \).

The fact that several atoms appear more than once in the \( Q = 3 \) shell indicates that six-membered rings exist (although they are not necessarily fundamental). Similarly, if two atoms in the \( Q = 3 \) shell were linked to each other (this does not occur in our example), this would indicate five-membered rings (again not necessarily fundamental). To determine whether a ring is fundamental, we compare minimal path distances to path distances along the ring (Marians and Hobbs, 1989b). The path distance between two \( T \) atoms is simply the number of \( T-T \) links traversed along any framework path connecting the two. Although there are an infinite number of such paths in an infinite framework, we are primarily interested in the minimal path distance, which can be found directly from the clusters. The minimal path distance between one \( T \) atom and a \( T \) atom in its \( Q \)th neighbor shell is equal to \( Q \). Thus, the minimal path distances between all pairs of \( T \) atoms in the entire structure are found from the clusters of the \( T \) atoms in the unit cell. Marians and Hobbs (1989b) have shown that a ring is fundamental if the shortest distance between any pair of \( T \) atoms along the ring is equal to its minimal path distance. Thus, the steps involved in determining a fundamental ring are (1) construct a potential ring by inspection of the cluster; (2) determine the shortest path distances along the ring, again by inspection of the ring; and (3) compare these path distances with minimal path distances. For the ring outlined in the cluster above:

\[
(1,0,0,0) - (2,0,-1,-1) - (1,-1,-1,0) \\
(3,0,-1,0) - (2,0,-1,0) - (3,-1,-1,0),
\]

we see that the shortest path distance along the ring between, for example, \((2,0,-1,-1)\) and \((2,0,-1,0)\) is three. From the cluster of atom \((2,0,0,0)\), we see that the minimal path distance between \((2,0,0,0)\) and \((2,0,0,1)\) is three, and thus the minimal path distance between \((2,0,-1,-1)\) and \((2,0,-1,0)\) is also three, the same as the shortest path distance along the ring. By checking all \( T \) atom pairs in the ring in this way, we would find that this particular six-membered ring is fundamental.