Rings, topology, and the density of tectosilicates

Lars Stixrude, 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 new low-density zeolites important to industry (Smith and Dytrych, 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, faujasite, 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 ge-

ometry 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

Framework	FD	L	FD*	Reference
ZSM-18	14.27	3.090	14.13	Lawton and Rohrbaugh (1990)
Linde-A	12.88	3.201	14.17	Gramlich and Meier (1970)
Rho	14.17	3.101	14.19	Robson et al. (1973)
Gmelinite	14.59	3.131	15.04	Fischer (1966)
Chabazite	14.47	3.141	15.06	Calligaris et al. (1982)
ZK-5	14.68	3.128	15.09	Meier and Kokotailo (1965)
Offretite	15.52	3.131	16.00	Gard and Tait (1972)
Erionite	15.64	3.136	16.19	Staples and Gard (1959)
Levyne	15.23	3.177	16.39	Merlino et al. (1975)
Linde-L	16.37	3.104	16.43	Barrer and Villiger (1969)
Phillipsite	15.82	3.144	16.50	Rinaldi et al. (1974)
Stilbite	16.29	3.125	16.68	Galli (1971)
Gismondine	15.29	3.197	16.77	Fischer (1963)
Heulandite	17.12	3.115	17.36	Alberti and Vezzalini (1983)
Laumontite	17.78	3.084	17.51	Bartl and Fischer (1967)
Mordenite	17.03	3.130	17.53	Meier (1961)
Losod	15.78	3.221	17.70	Sieber and Meier (1974)
Sodalite	17.20	3.136	17.81	Löns and Schulz (1967)
Cancrinite	16.58	3.179	17.87	Jarchow (1965)
Natrolite	17.73	3.111	17.92	Pechar et al. (1983)
Dachiardite	17.34	3.148	18.16	Gottardi and Meier (1963)
Epistilbite	17.65	3.133	18.22	Perotta (1967)
Dodecasil	18.47	3.111	18.68	Gerke and Gies (1984)
Melanophlogite	18.96	3.124	19.41	Gies (1983)
ZSM-22	19.73	3.092	19.57	Kokotailo et al. (1985)
ZSM-23	20.00	3.081	19.64	Rohrman et al. (1985)
ZSM-48	19.92	3.091	19.75	Schlenker et al. (1985)
Bikitaite	20.29	3.100	20.29	Kocman et al. (1974)
Paracelsian	21.45	3.090	21.24	Wyckoff (1982)
Tridymite	22.21	3.081	21.81	Wyckoff (1982)
Feldspar	22.25	3.096	22.16	Colville and Ribbe (1968)
CaGa$_2$O$_4$	21.49	3.131	22.14	Deiseroth and Müller-Buschbaum (1973)
Cristobalite	23.28	3.074	22.70	Peacor (1973)
CaAl$_2$Si$_2$O$_8$	23.36	3.075	22.80	Takéuchi et al. (1973)
Marialite	21.75	3.141	22.63	Levien and Papike (1976)
Banalsite	22.52	3.128	23.14	Haga (1973)
Cordierite	23.15	3.146	24.20	Cohen et al. (1977)
Quartz	26.52	3.057	25.43	Levien et al. (1980)
Coesite	29.28	3.086	28.87	Geisinger et al. (1987)

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$(L/L_s)^3$, where the standard T-T distance L_s is chosen to be 3.1 Å.
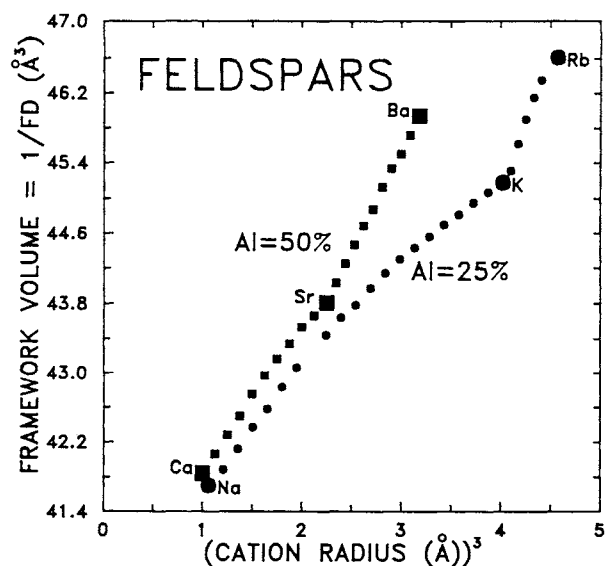

Fig. 1. Summary of density data for the feldspar framework type, plotted as the volume per T atom vs. the average radius cubed of the interstitial cations, taken from Shannon (1976). The alkali feldspar series is plotted as circles and the alkaline-earth series as squares. End-member compositions are indicated by enlarged symbols. The data from the Ca-Sr-Ba series are from Bambauer and Nager (1981), the Na-K series from Kroll et al. (1986), and the K-Rb series from McMillan et al. (1980). The difference between high (Al-Si disordered) and low (Al-Si ordered) structural states (not shown) is comparable to the size of the larger symbols. The total variation in framework volume (or framework density) shown is less than 12%, small compared with the variation among different framework types (Fig. 3).

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-
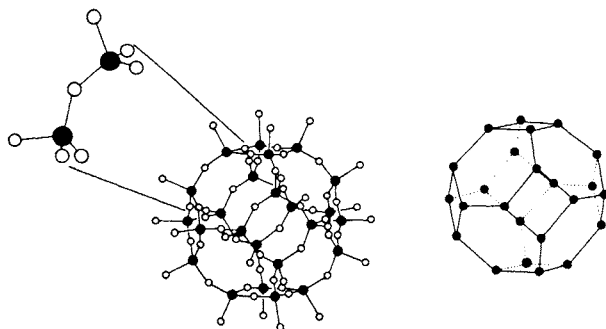
Fig. 2. Relationship between actual tectosilicate structure and the simplified conceptual structure used in this paper. On the left is the bitetrahedron, the largest structural unit shared by all tectosilicates, consisting of two T atoms (solid circles) surrounded by their coordinating O atoms (open circles). A portion of the sodalite structure, together with its simplified version (far right), derived by eliminating O atoms and interstitial cations and drawing links between T atoms that share a common O.
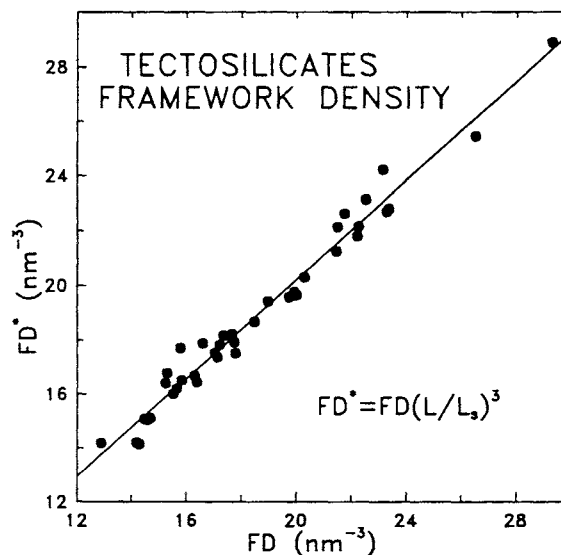

Fig. 3. The framework density of all the frameworks listed in Table 1 plotted against their framework density scaled to a standard T-T distance (L_s = 3.1 Å). This shows the wide variability of framework density among tectosilicates and the inability of variations in T-T distance (L) to account for this variability.

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 that the variability of FD* (FD scaled to a standard T-T distance) is 90% of the variability of FD itself. The inability of local geometries to explain framework densities provides the primary motivation for the examination of larger scale framework elements such as clusters and rings.

CLUSTERS

Clusters in tectosilicate framework structures are the physical expression of the coordination sequences first applied extensively to tectosilicates by Meier and Moeck (1979) and Brunner (1979). A cluster consists of a central T atom, the four T atoms linked to it, all the T atoms linked to these four and so on. The four T atoms linked to the central T atom are referred to as the first linked neighbors. All the T atoms linked to the first linked neighbors (except of course for the central T atom) are referred to as second linked neighbors. All the T atoms linked to the second linked neighbors (except the first linked neighbors) are referred to as third linked neighbors and so on. More specifically, for a cluster of size Q with numbers of first through Qth linked neighbors $N_1, N_2, N_3,$ ..., N_Q, the total number of T atoms in the cluster M_Q is given by:

$$M_Q = 1 + \sum_{i=1}^{Q} N_i. \tag{1}$$

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

$$N_Q = 4 \times 3^{Q-1} \tag{2}$$

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

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

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
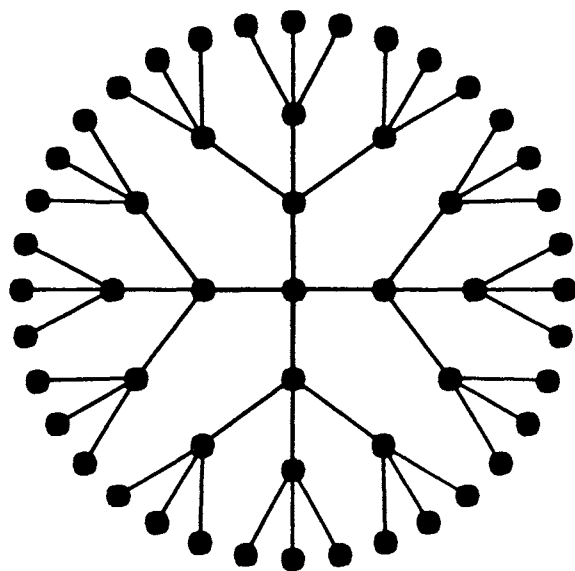
Fig. 4. Bethe lattice complete through the third linked neighbor shell.

TABLE 2. Cluster statistics

Framework	N_1	N_2	N_3	N_4	N_5	N_6
ZSM-18	4.000	9.529	17.294	29.294	45.176	65.412
Linde-A	4.000	9.000	17.000	28.000	42.000	60.000
Rho	4.000	9.000	17.000	28.000	42.000	60.000
Gmelinite	4.000	9.000	17.000	29.000	45.000	65.000
Chabazite	4.000	9.000	17.000	29.000	45.000	64.000
ZK-5	4.000	9.000	17.000	29.000	45.000	64.000
Offretite	4.000	9.333	18.000	30.667	48.667	72.000
Erionite	4.000	9.333	18.000	30.667	48.667	71.333
Levyne	4.000	9.333	18.000	30.667	48.000	68.667
Linde-L	4.000	9.333	18.333	31.000	47.000	68.000
Phillipsite	4.000	9.000	18.000	32.000	49.000	69.500
Stilbite	4.000	10.222	19.111	34.667	57.111	80.000
Gismondine	4.000	9.000	18.000	32.000	48.000	67.000
Heulandite	4.000	10.667	20.444	36.000	59.333	85.333
Laumontite	4.000	10.000	19.333	32.667	52.000	74.000
Mordenite	4.000	11.667	22.000	38.000	60.333	88.000
Losod	4.000	10.000	20.000	34.000	53.000	76.000
Sodalite	4.000	10.000	20.000	34.000	52.000	74.000
Cancrinite	4.000	10.000	20.000	34.000	54.000	78.000
Natrolite	4.000	8.800	18.800	35.200	52.800	75.600
Dachiardite	4.000	11.667	22.000	38.667	63.000	93.000
Epistilbite	4.000	11.667	22.000	39.333	64.333	92.333
Dodecasil	4.000	11.647	23.824	40.588	64.000	92.353
Melano-phlogite	4.000	12.000	24.783	42.261	67.652	98.000
ZSM-22	4.000	12.000	23.000	41.000	64.667	94.333
ZSM-23	4.000	12.000	23.000	41.167	65.000	95.167
ZSM-48	4.000	11.667	23.833	40.667	64.333	93.667
Bikitaite	4.000	12.000	24.000	42.667	69.333	98.667
Paracelsian	4.000	10.000	21.000	37.000	57.000	81.000
Tridymite	4.000	12.000	25.000	44.000	67.000	96.000
Feldspar	4.000	10.000	21.000	38.000	57.000	81.000
$CaGa_2O_4$	4.000	11.000	24.000	41.000	63.000	91.000
Cristobalite	4.000	12.000	24.000	42.000	64.000	92.000
$CaAl_2Si_2O_8$	4.000	11.000	24.000	41.000	62.000	90.000
Marialite	4.000	11.000	22.000	41.000	64.667	92.000
Banalsite	4.000	11.000	23.000	42.000	66.000	97.000
Cordierite	4.000	10.667	23.333	44.667	66.000	102.000
Quartz	4.000	12.000	30.000	52.000	80.000	116.000
Coesite	4.000	10.000	22.500	47.000	83.000	126.000

Note: N_Q is the mean number of neighbors in the Qth linked neighbor shell of a single T atom averaged over all T atoms in the structure.

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

$$FD = (M_{Q-1} + \tfrac{1}{2}N_Q)/V(D_Q) \qquad (4)$$

where

$$V(D_Q) = 4\pi D_Q^3/3. \qquad (5)$$

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%. We chose $Q = 6$ since this is the smallest cluster size that contains all the fundamental rings of the framework structures examined here (see Table 4 and discussion of rings below). For much larger Q, the approximation that only atoms in the Qth shell are shared will become less accurate, whereas for a much smaller Q, different frameworks become indistinct: in the limit of $Q = 1$, 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_Q), rather than geometric measures (D_Q), of cluster size are primar-

ily responsible for the observed variation in framework density. There is, for example, a good correlation between cluster population (M_6) and framework density (Fig. 6). Similar correlations between N_Q and FD have been observed by several previous authors using slightly different data sets (Brunner, 1979; Akporiaye and Price, 1989). In contrast, Figure 7 shows that the geometry of clusters, as measured by D_Q, is nearly independent of framework type. The standard deviation of D_6 for all framework structures is only 10%. An explanation of variations in the topological size of clusters, and thus framework density, is therefore of primary importance. In the next section we show that variations in ring statistics provide this explanation.

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

TABLE 3. Cluster geometry

Framework	D_1	D_2	D_3	D_4	D_5	D_6
ZSM-18	3.090	5.082	7.210	9.350	11.398	13.470
Linde-A	3.201	5.307	7.504	9.504	11.524	13.609
Rho	3.101	5.215	7.286	9.217	11.216	13.179
Gmelinite	3.131	5.210	7.251	9.231	11.222	13.228
Chabazite	3.141	5.243	7.332	9.310	11.267	13.223
ZK-5	3.128	5.195	7.229	9.235	11.195	13.114
Offretite	3.131	5.176	7.173	9.187	11.240	13.254
Erionite	3.136	5.176	7.168	9.163	11.200	13.187
Levyne	3.177	5.269	7.274	9.231	11.221	13.223
Linde-L	3.104	5.089	6.936	8.810	10.893	13.024
Phillipsite	3.144	5.237	7.279	9.121	11.062	13.173
Stilbite	3.125	5.059	7.236	9.359	11.332	13.388
Gismondine	3.197	5.330	7.377	9.238	11.213	13.373
Heulandite	3.115	5.058	7.231	9.324	11.272	13.399
Laumontite	3.084	5.096	6.993	9.010	10.946	12.860
Mordenite	3.130	5.067	7.325	9.403	11.507	13.682
Losod	3.221	5.350	7.355	9.356	11.420	13.508
Sodalite	3.136	5.232	7.132	9.084	11.050	13.089
Cancrinite	3.179	5.240	7.222	9.209	11.285	13.306
Natrolite	3.111	5.169	7.109	8.726	10.828	12.996
Dachiardite	3.148	5.095	7.353	9.441	11.506	13.685
Epistilbite	3.133	5.071	7.322	9.396	11.419	13.646
Dodecasil	3.111	5.087	7.192	9.248	11.390	13.549
Melanophlogite	3.124	5.090	7.222	9.284	11.382	13.623
ZSM-22	3.092	4.999	7.040	9.097	11.225	13.335
ZSM-23	3.081	4.978	7.007	9.061	11.184	13.274
ZSM-48	3.091	5.026	6.950	9.098	11.151	13.301
Bikitaite	3.100	5.028	7.091	9.126	11.188	13.423
Paracelsian	3.090	5.031	6.834	8.594	10.496	12.503
Tridymite	3.081	5.031	6.845	8.908	10.921	13.027
Feldspar	3.096	5.030	6.841	8.595	10.504	12.577
CaGa$_2$O$_4$	3.131	5.110	6.893	8.844	10.889	12.922
Cristobalite	3.074	4.978	6.732	8.740	10.666	12.728
CaAl$_2$Si$_2$O$_8$	3.075	4.984	6.723	8.593	10.569	12.557
Marialite	3.141	5.043	7.003	8.748	10.776	12.926
Banalsite	3.128	5.100	6.926	8.829	10.807	12.980
Cordierite	3.146	5.061	6.805	8.585	10.810	12.770
Quartz	3.057	4.953	6.710	8.689	10.867	12.931
Coesite	3.086	5.037	6.822	8.402	10.176	12.405

Note: D_Q is the mean distance from a single T atom to neighbors in its Qth linked neighbor shell averaged over all T atoms in the structure.
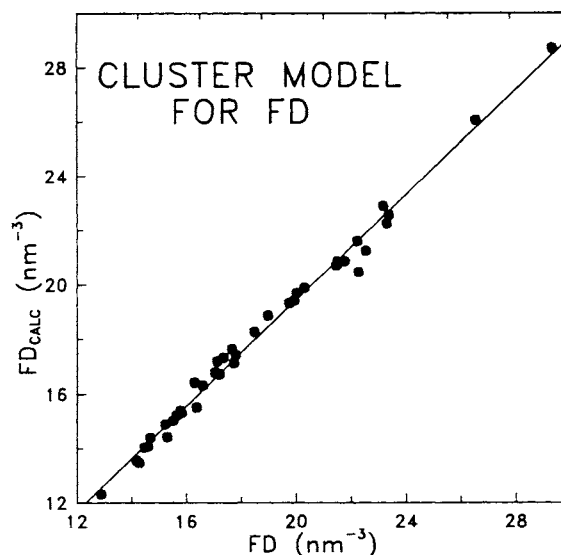

Fig. 5. Illustration of the excellent agreement between observed framework density and that predicted by the simple model relating cluster density to macroscopic density, which is described in the text (Eq. 4).

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
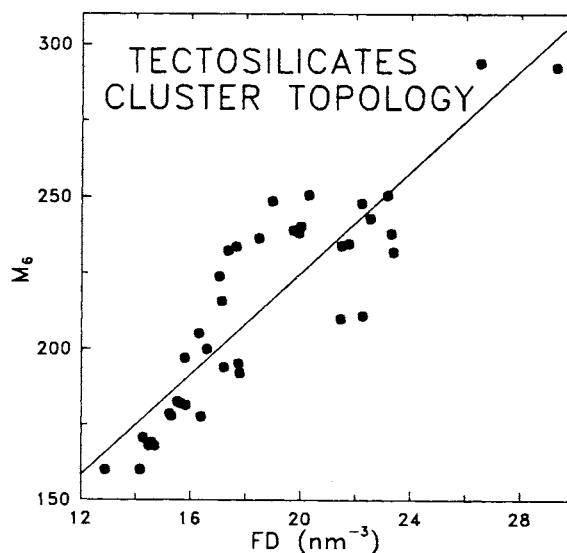
than the coordination numbers so profitably employed in describing ionic and metallic materials, should be the primary topological measure of covalently bonded structures. Thus, the characterization of physical models of silica glass built shortly thereafter (Evans and King, 1966; Bell and Dean, 1966) 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.

In the most general sense, a ring may be taken as any returning 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

Fig. 6. Plot showing the good correlation ($r = 0.88$) between the cluster population (M_6) and framework density, indicating that most of the variation in cluster density is accounted for by changes in the number of T atoms in a cluster rather than by changes in geometric size.
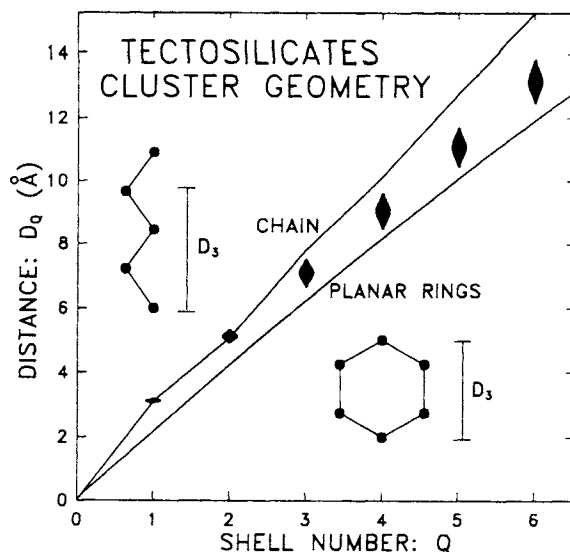
Fig. 7. Summary of cluster geometry in tectosilicates, showing the average distance to each of the first six linked neighbor shells for all frameworks listed in Table 1. The horizontal width of the symbols shown for each D_Q (pairs of Gaussian curves drawn out to ± twice the standard deviation) is proportional to the probability of finding a framework with a particular value of D_Q. The observed D_Q values are compared with two limiting cases: (1) D_Q expected if every atom in the Qth linked neighbor shell closed a planar ring of size $2Q$, and (2) D_Q expected if every atom in the Qth shell lay at the end of a chain of length Q with T-T-T angles equal to the ideal tetrahedral angle of 109.47°. The total variation in D_Q values is small compared with variations in cluster density (Fig. 6) and compared with the two limiting cases shown, indicating that cluster geometry is approximately independent of framework type.

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
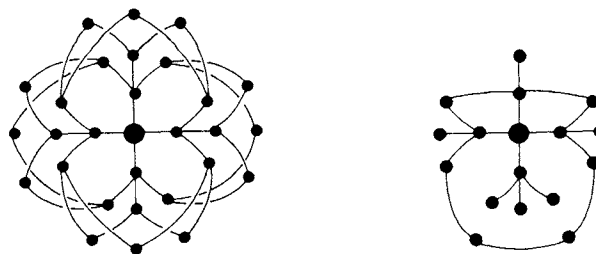

Fig. 8. On the left is a schematic representation of a portion of the cristobalite structure showing the 12 fundamental six-membered rings that pass through each T atom (after Marians and Hobbs, 1989a). The older definition of a fundamental ring (see text) allows only six rings to pass through any T atom. On the right is a schematic representation of a portion of a hypothetical framework. The older definition of fundamental rings would consider as fundamental the two four-membered rings and the six-membered ring. The definition used in this paper also counts the two four-membered rings but counts the seven-membered ring instead of the six-membered ring, since the latter can be divided into two smaller rings (see also Smith, 1978). Note that each structure shown is complete through the second linked neighbor shell of the enlarged central atom and, for clarity, includes only those third linked neighbors that close rings; in the case of cristobalite, this is half of the 24 total third linked neighbors.

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_Q, N_Q) and not geometry (D_Q). 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

Framework	3	4	5	6	7	8	9	10	11	12	K^*
ZSM-18	0.18	2.12	1.76	0.71	1.24	0.00	0.00	0.00	0.00	0.71	4.48
Linde-A	0.00	3.00	0.00	5.00	0.00	1.00	0.00	0.00	0.00	8.00	4.94
Rho	0.00	3.00	0.00	1.00	0.00	2.00	0.00	10.00	0.00	0.00	4.96
Gmelinite	0.00	3.00	0.00	1.00	0.00	6.00	0.00	0.00	0.00	7.00	4.98
Chabazite	0.00	3.00	0.00	1.00	0.00	6.00	0.00	0.00	0.00	1.00	4.86
ZK-5	0.00	3.00	0.00	1.00	0.00	6.00	0.00	0.00	0.00	0.00	4.83
Offretite	0.00	2.67	0.00	2.00	0.00	4.00	0.00	3.33	0.00	9.33	5.19
Erionite	0.00	2.67	0.00	2.00	0.00	4.00	0.00	3.33	0.00	5.33	5.10
Levyne	0.00	2.67	0.00	2.00	0.00	4.00	0.00	0.00	0.00	1.33	4.85
Linde-L	0.00	2.67	0.00	1.67	0.00	6.67	0.00	6.67	0.00	0.33	5.33
Phillipsite	0.00	3.00	0.00	0.00	0.00	4.00	0.00	5.00	0.00	0.00	4.80
Stilbite	0.00	1.78	2.22	4.00	0.00	2.22	0.00	1.11	0.00	0.00	5.11
Gismondine	0.00	3.00	0.00	0.00	0.00	4.00	0.00	0.00	0.00	0.00	4.52
Heulandite	0.00	1.33	3.33	1.33	0.00	1.33	0.00	1.11	0.00	2.00	4.98
Laumontite	0.00	2.00	0.00	6.00	0.00	2.67	0.00	3.33	0.00	20.00	5.69
Mordenite	0.00	0.33	5.00	0.00	0.00	2.00	0.00	3.33	0.00	1.00	5.33
Losod	0.00	2.00	0.00	4.00	0.00	0.00	0.00	5.00	0.00	14.00	5.40
Sodalite	0.00	2.00	0.00	4.00	0.00	0.00	0.00	0.00	0.00	32.00	5.56
Cancrinite	0.00	2.00	0.00	4.00	0.00	0.00	0.00	10.00	0.00	20.00	5.74
Natrolite	0.00	4.00	0.00	0.00	0.00	12.80	7.20	0.00	0.00	0.00	5.32
Dachiardite	0.00	0.33	5.00	0.00	0.00	1.33	0.00	6.67	0.00	3.67	5.51
Epistilbite	0.00	0.33	5.00	0.00	0.00	1.33	0.00	3.33	0.00	0.00	5.23
Dodecasil	0.00	0.35	4.41	1.24	0.00	0.00	0.00	5.29	0.00	0.00	5.33
Melanophlogite	0.00	0.00	5.22	0.78	0.00	0.00	0.00	2.61	0.00	0.00	5.25
ZSM-22	0.00	0.00	3.33	5.00	0.00	0.00	0.00	1.67	0.00	0.00	5.58
ZSM-23	0.00	0.00	3.33	5.00	0.00	0.00	0.00	1.67	0.00	0.00	5.58
ZSM-48	0.00	0.33	1.67	7.50	0.00	1.33	0.00	0.83	0.00	0.00	5.72
Bikitaite	0.00	0.00	3.33	4.00	0.00	2.67	0.00	0.00	0.00	0.00	5.67
Paracelsian	0.00	2.00	0.00	3.00	0.00	8.00	0.00	0.00	0.00	0.00	5.43
Tridymite	0.00	0.00	0.00	12.00	0.00	0.00	0.00	0.00	0.00	0.00	6.00
Feldspar	0.00	2.00	0.00	4.50	0.00	5.00	0.00	22.50	0.00	0.00	6.09
CaGa$_2$O$_4$	0.00	1.00	0.00	6.00	0.00	16.00	0.00	0.00	0.00	0.00	6.33
Cristobalite	0.00	0.00	0.00	12.00	0.00	0.00	0.00	0.00	0.00	0.00	6.00
CaAl$_2$Si$_2$O$_8$	0.00	1.00	0.00	6.00	0.00	20.00	0.00	0.00	0.00	0.00	6.47
Marialite	0.00	1.00	3.33	2.00	0.00	5.33	0.00	3.33	0.00	0.00	5.51
Banalsite	0.00	1.00	0.00	10.50	0.00	2.00	0.00	10.00	0.00	0.00	5.99
Cordierite	0.00	1.33	0.00	4.67	0.00	0.00	40.00	6.67	0.00	0.00	6.93
Quartz	0.00	0.00	0.00	6.00	0.00	40.00	0.00	0.00	0.00	0.00	7.38
Coesite	0.00	2.00	0.00	1.50	0.00	2.00	9.00	2.50	11.00	9.00	6.00

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 tree of size Q, the number of T atoms pruned from the tree, $P(Q,K)$ by the formation of a ring of size K is:

$$P(Q,K) = 2 \times \sum_{i=0}^{Q-S-1} 3^i = 3^{Q-S} - 1 \qquad (6)$$

for odd-membered rings and

$$P(Q,K) = 1 + 4 \times \sum_{i=0}^{Q-S-1} 3^i = 2 \times 3^{Q-S} - 1 \qquad (7)$$

for even-membered rings, where S is the linked neighbor shell in which a ring closes: S is $1/2(K - 1)$ for odd rings and $1/2K$ for even rings. We define the relative pruning efficiency, $P^*(K)$ as the large Q limit of $P(Q,K)$ normalized to $P(Q,3)$:

$$P^*(K) = \lim_{Q \to \infty} P(Q,K)/P(Q,3). \qquad (8)$$

Thus, for odd-membered rings:

$$P^*(K) = 1/3^{1/2(K-3)} \qquad (9)$$

and for even-membered rings:

$$P^*(K) = 2/3^{1/2(K-2)}. \qquad (10)$$

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:

$$K^* = \Sigma \, K\mathrm{f}(K)\mathrm{W}(K)/\Sigma \, \mathrm{f}(K)\mathrm{W}(K), \qquad (11)$$

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.
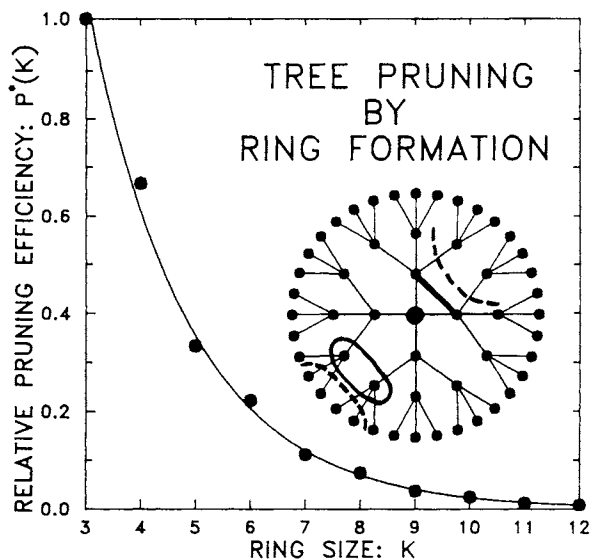
Fig. 9. The effect of ring formation on framework density. The inset shows a cluster of size 3 from the Bethe lattice, with T atoms indicated by symbols and T-T links indicated by light lines. The bold lines indicate the effect of ring formation. In the upper right portion of the cluster, a three-membered ring is formed by linking two T atoms in the first linked neighbor shell, as shown by the solid bold line. The dashed bold line indicates the pruning required by the constraint of four-coordination. Similarly, in the bottom left portion of the cluster, a four-membered ring is formed by equating two T atoms in the second linked neighbor shell, indicated by the bold line encircling the two T atoms. Again, the bold dashed line indicates the portions of the cluster that must be pruned to maintain four-coordination. The large circles plotted are the relative pruning efficiencies for different-sized rings from Equations 9 and 10. The line is an exponential fit to guide the eye. The plot shows that small rings have a much greater effect on framework density than large ones.

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_Q 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 (Marians 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
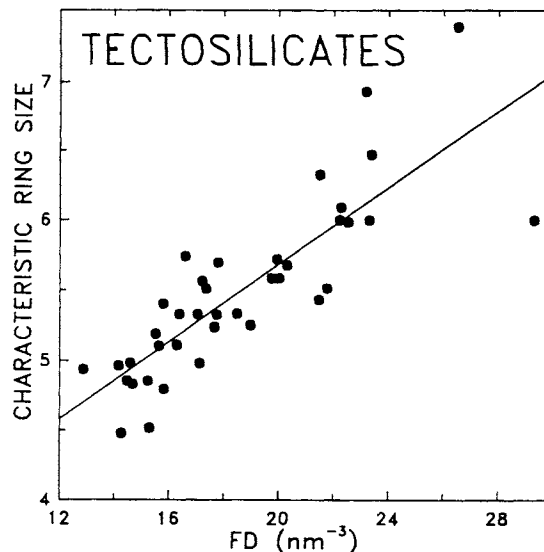

Fig. 10. Plot showing the positive correlation ($r = 0.83$) between characteristic ring size, K^* (Eq. 11), and framework density (FD) as predicted by the theory of the effects of ring formation on framework density described in the text and summarized in Figure 9.
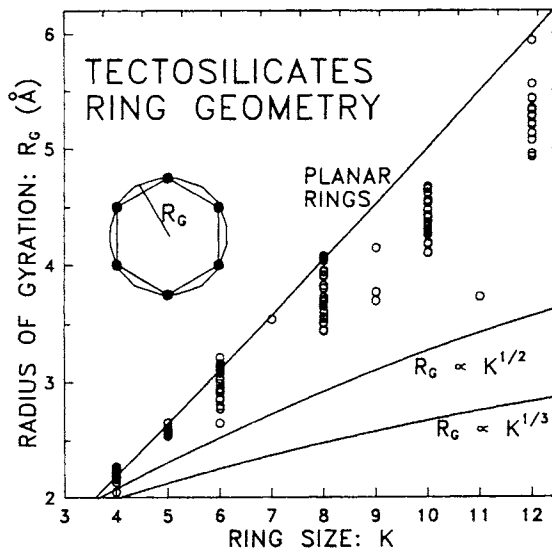

Fig. 11. Geometry of rings in tectosilicates as measured by the radius of gyration (Eq. 13) and illustrated schematically in the upper left portion of the figure. Each symbol represents the average radius of gyration for all rings of size K in one structure. The single example of three-membered rings (in ZSM-18; $R_G = 1.7419$) is not shown for convenience. Observed values are compared with two limiting cases: (1) planar rings, for which R_G is a maximum and (2) the value of R_G expected if the effective density of rings (Eq. 12) remained constant with increasing ring size starting at $K = 3$. The two lower curves correspond to effective ring dimensionalities of 3 (lowermost curve) and 2 (see Eq. 15). All R_G values are scaled to a standard T-T distance of 3.1 Å to facilitate comparison.

density of a ring:

$$\rho(K) \propto K/R_G^d, \qquad (12)$$

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

$$R_G^2 = (1/2K^2) \sum_{i,j} r_{ij}^2, \qquad (13)$$

where r_{ij} is the distance between T atoms i and j and d is the 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_G for all the rings of this study and compared these values to the value of R_G for planar rings:

$$R_G \text{ (Planar)} = 1/2L\csc(\pi/K), \qquad (14)$$

where L is the T-T distance, and to variations in R_G for constant effective ring density:

$$R_G[\rho(K) = \text{constant}] \propto K^{1/d}. \qquad (15)$$

Figure 11 shows that, although rings deviate systematically from planarity with increasing ring size, the fact that R_G 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 struc-

ture caused by increasing pressure (Stixrude and Bukowinski, 1990).

REFERENCES CITED

Akporiaye, D.E., and Price, G.D. (1989) Relative stability of zeolite frameworks from calculated energetics of known and theoretical structures. Zeolites, 9, 321–328.

Alberti, A., and Vezzalini, G. (1983) Thermal behavior of heulandites: A structural study of the dehydration of Nadap heulandite. Tschermaks' Mineralogische und Petrologische Mitteilungen, 31, 259–270.

Bambauer, H.U., and Nager, H.E. (1981) Gitterkonstanten und displazive Transformation synthetischer Erdalkalifeldspäte I. System Ca[Al$_2$Si$_2$O$_8$]-Sr[Al$_2$Si$_2$O$_8$]-Ba[Al$_2$Si$_2$O$_8$]. Neues Jahrbuch für Mineralogie Abhandlungen, 141, 225–239.

Barrer, R. M., and Villiger, H. (1969) The crystal structure of the synthetic zeolite L. Zeitschrift für Kristallographie, 128, 253–370.

Bartl, H., and Fischer, K. (1967) Untersuchung der Kristallstruktur des Zeolithes Laumontit. Neues Jahrbuch für Mineralogie Monatshefte, 1967, 33–42.

Belch, A.C., and Rice, S.A. (1987) The distribution of rings of hydrogen-bonded molecules in a model of liquid water. Journal of Chemical Physics, 86, 5676–5682.

Bell, R.J., and Dean, P. (1966) Properties of vitreous silica: Analysis of random network models. Nature, 212, 1354–1355.

Bernal, J.D. (1964) The structure of liquids. Proceedings of the Royal Society of London, Series A, 280, 299–322.

Bethe, H.A. (1935) Statistical theory of superlattices. Proceedings of the Royal Society of London, Series A, 150, 552–575.

Brunner, G.O. (1979) The properties of coordination sequences and conclusions regarding the lowest possible density of zeolites. Journal of Solid State Chemistry, 29, 41–45.

Brunner, G.O., and Meier, W.M. (1989) Framework density distribution of zeolite-type tetrahedral nets. Nature, 337, 146–147.

Calligaris, M., Nardin, G., and Randaccio, L. (1982) Cation-site location in a natural chabazite. Acta Crystallographica, B38, 602–605.

Cohen, J.P., Ross, F.K., and Gibbs, G.V. (1977) An X-ray and neutron diffraction study of hydrous low cordierite. American Mineralogist, 62, 67–78.

Colville, A.A., and Ribbe, P.H. (1968) The crystal structure of an adularia and a refinement of the structure of orthoclase. American Mineralogist, 53, 25–37.

Davis, M.E., Saldarriaga, C., Montes, C., Garces, J., and Crowder, C. (1988) A molecular sieve with eighteen-membered rings. Nature, 331, 698–699.

Deiseroth, H.J., and Müller-Buschbaum, H.K. (1973) Die Kristallstruktur von monoklinem CaGa$_2$O$_4$. Zeitschrift für Anorganische und Allgemeine Chemie, 402, 201–205.

Domb, C. (1960) On the theory of cooperative phenomena in crystals. Advances in Physics, 9, 245–295.

Evans, D.L., and King, S.V. (1966) Random network model of vitreous silica. Nature, 212, 1353–1354.

Fischer, K. (1963) The crystal structure determination of the zeolite gismondite CaAl$_2$Si$_2$O$_8$·4H$_2$O. American Mineralogist, 48, 664–672.

——— (1966) Untersuchung der Kristallstruktur von Gmelinit. Neues Jahrbuch für Mineralogie Monatshefte, 1966, 1–13.

Galli, E. (1971) Refinement of the crystal structure of stilbite. Acta Crystallographica, B27, 833–841.

Gard, J.A., and Tait, J.M. (1972) The crystal structure of the zeolite offretite, K$_{1.1}$Ca$_{1.1}$Mg$_{0.7}$(Si$_{12.8}$Al$_{5.2}$O$_{36}$)·15·2H$_2$O. Acta Crystallographica, B28, 825–834.

Geisinger, K., Spackman, M.A., and Gibbs, G.V. (1987) Exploration of

structure, electron density distribution and bonding in coesite with Fourier and pseudoatom refinement methods using single-crystal x-ray diffraction data. Journal of Physical Chemistry, 91, 3237–3244.

Gerke, H., and Gies, H. (1984) Studies on clathrasils. IV. Crystal structure of dodecasil 1H, a synthetic clathrate compound of silica. Zeitschrift für Kristallographie, 166, 11–22.

Gies, H. (1983) Studies on clathrasils. III. Crystal structure of melanophlogite, a natural clathrate compound of silica. Zeitschrift für Kristallographie, 164, 247–257.

Gottardi, G., and Meier, W.M. (1963) The crystal structure of dachiardite. Zeitschrift für Kristallographie, 119, 53–64.

Gramlich, V., and Meier, W.M. (1970) The crystal structure of hydrated NaA: A detailed refinement of a pseudosymmetric zeolite structure. Zeitschrift für Kristallographie, 133, 134–149.

Haga, N. (1973) The crystal structure of banalsite, $BaNa_2Al_4Si_4O_{12}$, and its relation to the feldspar structure. Mineralogical Journal, 7, 262–281.

Hurlbut, C.S., and Klein, C. (1977) Manual of mineralogy (19th edition), 532 p. Wiley, New York.

Jarchow, O. (1965) Atomanordnung und Strukturverfeinerung von Cancrinit. Zeitschrift für Kristallographie, 122, 407–422.

King, S.V. (1967) Ring configurations in a random network model of vitreous silica. Nature, 213, 1112–1113.

Kittel, C. (1976) Introduction to solid state physics, 608 p. Wiley, New York.

Kocman, V., Gait, R.I., and Rucklidge, J. (1974) The crystal structure of bikitaite, $Li(AlSi_2O_6)H_2O$. American Mineralogist, 59, 71–78.

Kokotailo, G.T., Schlenker, J.L., Dwyer, F.G., and Valyocsik, E.W. (1985) The framework topology of ZSM-22: A high silica zeolite. Zeolites, 5, 349–351.

Kroll, H., Schmiemann, I., and von Cölln, G. (1986) Feldspar solid solutions. American Mineralogist, 71, 1–16.

Lawton, S.L., and Rohrbaugh, W.J. (1990) The framework topology of ZSM-18, a novel zeolite containing rings of three (Si,Al)-O species. Science, 247, 1319–1322.

Levien, L., and Papike, J.J. (1976) Scapolite crystal chemistry: Aluminum-silicon distributions, carbonate group disorder, and thermal expansion. American Mineralogist, 61, 864–877.

Levien, L., Prewitt, C.T., and Weidner, D.J. (1980) Structure and elastic properties of quartz at pressure. American Mineralogist, 65, 920–930.

Liebau, F. (1988) Structural similarities and dissimilarities between SiO_2 and H_2O. In R.A.B. Devine, Ed., The physics and technology of amorphous SiO_2, p. 15–35. Plenum Press, New York.

Löns, J., and Schulz, H. (1967) Strukturverfeinerung von Sodalith, $Na_8Si_6Al_6O_{24}Cl_2$. Acta Crystallographica, 23, 434–436.

Marians, C.S., and Hobbs, L.W. (1989a) The phase structure of aperiodic SiO_2 as a function of network topology. Journal of Non-crystalline Solids, 106, 309–312.

———(1989b) Network properties of crystalline polymorphs of silica. Journal of Non-crystalline Solids, in press.

McMillan, P.F., Brown, W.L., and Openshaw, R.E. (1980) The unit-cell parameters of an ordered K-Rb alkali feldspar series. American Mineralogist, 65, 458–464.

Meier, W.M. (1961) The crystal structure of mordenite (ptilolite). Zeitschrift für Kristallographie, 115, 439–450.

———(1986) Zeolites and zeolite-like materials. In Y. Murakami, A. Iijima, and J.W. Ward, Eds., New developments in zeolite science and technology: Proceedings of the 7th International Zeolite Conference, p. 13–22. Elsevier, Amsterdam.

Meier, W.M., and Kokotailo, G.T. (1965) The crystal structure of synthetic zeolite ZK-5. Zeitschrift für Kristallographie, 121, 211–219.

Meier, W.M., and Moeck, H.J. (1979) The topology of three-dimensional 4-connected nets: Classification of zeolite framework types using coordination sequences. Journal of Solid State Chemistry, 27, 349–355.

Meier, W.M., and Olson, D.H. (1988) Atlas of zeolite structure types, 166 p. Butterworths, Kent, England.

Merlino, S., Galli, E., and Alberti, A. (1975) The crystal structure of levyne. Tschermaks' Mineralogische und Petrologische Mitteilungen, 22, 117–129.

Peacor, D.R. (1973) High-temperature single-crystal study of the cristobalite inversion. Zeitschrift für Kristallographie, 138, 274–298.

Pechar, F., Schaefer, W., and Will, G. (1983) A neutron diffraction refinement of the crystal structure of natural natrolite, $Na_2Al_2Si_3O_{10}2H_2O$. Zeitschrift für Kristallographie, 164, 19–24.

Perrotta, A.J. (1967) The crystal structure of epistilbite. Mineralogical Magazine, 36, 480–490.

Rinaldi, R., Pluth, J.J., and Smith, J.V. (1974) Zeolites of the phillipsite family. Refinements of the crystal structures of phillipsite and harmotome. Acta Crystallographica, B30, 2426–2433.

Robson, H.E., Shoemaker, D.P., Ogilvie, R.A., and Manor, P.C. (1973) Synthesis and crystal structure of zeolite rho—A new zeolite related to Linde type A. Advances in Chemistry Series, 121, 106–115.

Rohrman, A.C., Jr., LaPierre, R.B., Schlenker, J.L., Wood, J.D., Valyocsik, E.W., Rubin, M.K., Higgins, J.B., and Rohrbaugh, W.J. (1985) The framework topology of ZSM-23: A high silica zeolite. Zeolites, 5, 352–354.

Schlenker, J.L., Rohrbaugh, W.J., Chu, P., Valyocsik, E.W., and Kokotailo, G.T. (1985) The framework topology of ZSM-48: A high silica zeolite. Zeolites, 5, 355–358.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica, A32, 751–767.

Sieber, W., and Meier, W.M. (1974) Formation and properties of Losod, a new sodium zeolite. Helvetica Chimica Acta, 57, 1533–1549.

Smith, J.V. (1977) Enumeration of 4-connected 3-dimensional nets and classification of framework silicates. I. Perpendicular linkage from simple hexagonal net. American Mineralogist, 62, 703–709.

———(1978) Enumeration of 4-connected 3-dimensional nets and classification of framework silicates, II. Perpendicular and near-perpendicular linkages from 4.8^2, 3.12^2, and $4.6.12$ nets. American Mineralogist, 63, 960–969.

———(1979) Enumeration of 4-connected 3-dimensional nets and classification of framework silicates, III. Combination of helix, and zigzag, crankshaft and saw chains with simple 2D nets. American Mineralogist, 64, 551–562.

———(1982) Geometrical and structural crystallography, 450 p. Wiley, New York.

Smith, J.V., and Bennett, J.M. (1981) Enumeration of 4-connected 3-dimensional nets and classification of framework silicates: The infinite set of ABC-6 nets; the Archimedean and σ-related nets. American Mineralogist, 66, 777–788.

———(1984) Enumeration of 4-connected 3-dimensional nets and classification of framework silicates: Linkages from the two $(5^2.8)_2(5.8^2)_1$ 2D nets. American Mineralogist, 69, 104–111.

Smith, J.V., and Brown, W.L. (1988) Feldspar minerals (vol. 1, 2nd edition), 828 p. Springer-Verlag, Berlin.

Smith, J.V., and Dytrych, W.J. (1984) Nets with channels of unlimited diameter. Nature, 309, 607–608.

Staples, L.W., and Gard, J.A. (1959) The fibrous zeolite erionite; its occurrence, unit cell, and structure. Mineralogical Magazine, 32, 261–281.

Stishov, S.M., and Popova, S.V. (1961) New dense polymorphic modification of silica. Geokhimiya, 10, 837–839.

Stixrude, L., and Bukowinski, M.S.T. (1988) Simple covalent potential models of tetrahedral SiO_2: Applications to α-quartz and coesite at pressure. Physics and Chemistry of Minerals, 16, 199–206.

———(1989) Compression of tetrahedrally bonded SiO_2 liquid and silicate liquid-crystal density inversion. Geophysical Research Letters, 16, 1403–1406.

———(1990) A novel topological compression mechanism in a covalent liquid. Science, 250, 541ff.

Takéuchi, Y., Haga, N., and Ito, J. (1973) The crystal structure of monoclinic $CaAl_2Si_2O_8$: A case of monoclinic structure closely simulating orthorhombic symmetry. Zeitschrift für Kristallographie, 137, 380–398.

Wyckoff, R.W.G. (1982) Crystal structures, (2nd edition). Krieger Publishing Co., Malabar, Florida.

Zachariasen, W.H. (1932) The atomic arrangement in glass. Journal of the American Chemical Society, 54, 3841–3851.

APPENDIX 1. MEASUREMENT OF CLUSTER AND RING STATISTICS

The description of the algorithm for finding cluster parameters, N_Q and M_Q, and ring statistics, f(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** = i**a** + j**b** + k**c**, 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 (i1,0,0,0) is linked to (i2,1,0,1), then (i1,0 + j',0 + k',0 + l') is linked to (i2,1 + 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:

T atom	Atomic coordinates (u = 0.4697)
(1,0,0,0)	(u,0,0)
(2,0,0,0)	(0,u,2/3)
(3,0,0,0)	($-u$,$-u$,1/3),

then the resulting linkage table is

T atom	Linked to
(1,0,0,0)	(2,0,-1,-1), (2,1,0,-1), (3,0,-1,0), (3,0,0,0)
(2,0,0,0)	(1,-1,0,1), (1,0,1,1), (3,-1,0,0), (3,0,0,0)
(3,0,0,0)	(1,0,0,0), (1,0,1,0), (2,0,0,0), (2,1,0,0).

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 (2,0,0-1,0-1) are (1,−1,0-1,1-1), (1,0,1-1,1-1), (3,−1,0-1,0-1), and (3,0,0-1,0-1). Once the cluster is constructed, the number of distinct neighbors in each neighbor shell are counted to give N_Q and M_Q.

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
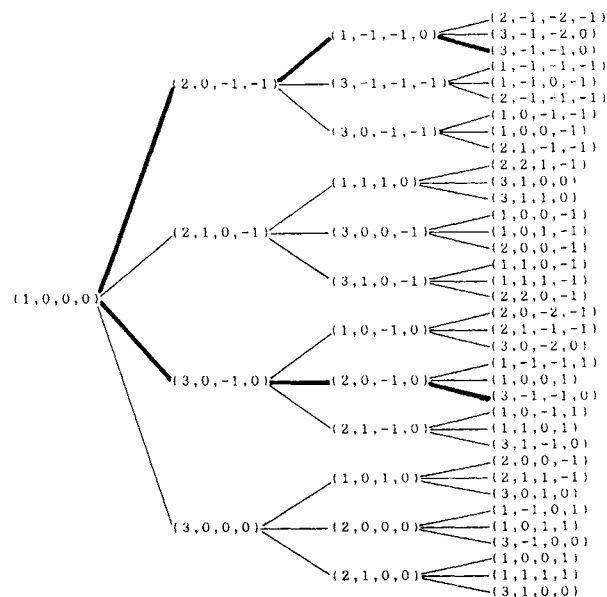

Fig. 1A. The cluster of atom (1,0,0,0) in quartz up to Q = 3. The bold lines indicate a fundamental six-membered ring.

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 Qth 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:

$$(1,0,0,0) - (2,0,-1,-1) - (1,-1,-1,0)$$
$$| \qquad\qquad\qquad\qquad\qquad |$$
$$(3,0,-1,0) - (2,0,-1,0) - (3,-1,-1,0),$$

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.