

# Hypothetical molecular sieve frameworks

Jacek Klinowski

There are various ways to describe the frameworks of molecular sieves and their enumeration. As the number of possible three-dimensional 4-connected nets is infinite, all enumerations reported so far have been derived by empirical methods, although many interesting and potentially viable structures, particularly with low framework density (rich in 3- and 4-membered rings), have been found as a result. It is likely that recent progress in mathematical tiling theory will lead to new advances in systematic enumeration not only of molecular sieves, but also of a variety of chemical structures.

## Addresses

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK; e-mail: jk18@cam.ac.uk

**Current Opinion in Solid State & Materials Science** 1998, 3:79–85

Electronic identifier: 1359-0286-003-00079

© Current Chemistry Ltd ISSN 1359-0286

## Abbreviations

**FD** framework density  
**SBU** secondary building unit  
**T-atoms** Si, Al and P atoms

## Introduction

The contrast between the small number of physical laws and the enormous number of structures to which these laws give rise is an intriguing aspect of the natural world. The handful of rules of chemical bonding results in many thousands of crystalline inorganic compounds with a bewildering number of different structures, even when only a few chemical elements are involved. For example, about a half of all known minerals are silicates with distinct structures, although their frameworks are built only of Si and O (plus Al in the case of aluminosilicates). Enumeration of networks of atoms in inorganic structures is a matter of considerable interest, but a formidable task for a scientist, as the number of three-dimensional nets is infinite. Derivation of chemically viable hypothetical networks is particularly desirable for microporous molecular sieves, of which there are now 105 recognized structure types, with several new ones being added to the list every year [1]. Molecular sieves, particularly zeolites, are widely applied as catalysts, sorbents and ion-exchangers. The annual industrial consumption of zeolites is  $\approx 550,000$  tonnes, of which 135,000 tonnes are used in catalysis, 375,000 as ion-exchangers in detergent powders and 40,000 as sorbents. New wide-pore ( $> 2$  nm) molecular sieves are much in demand, and a systematic and reliable enumeration procedure would not only reveal possible further structures, but could also assist in the design of new synthetic routes by using suitable 'structure-directing' molecules. It is noted that in this context that the use of nonaqueous media for the synthesis of molecular sieves has barely been explored.

## The structure of crystalline molecular sieves

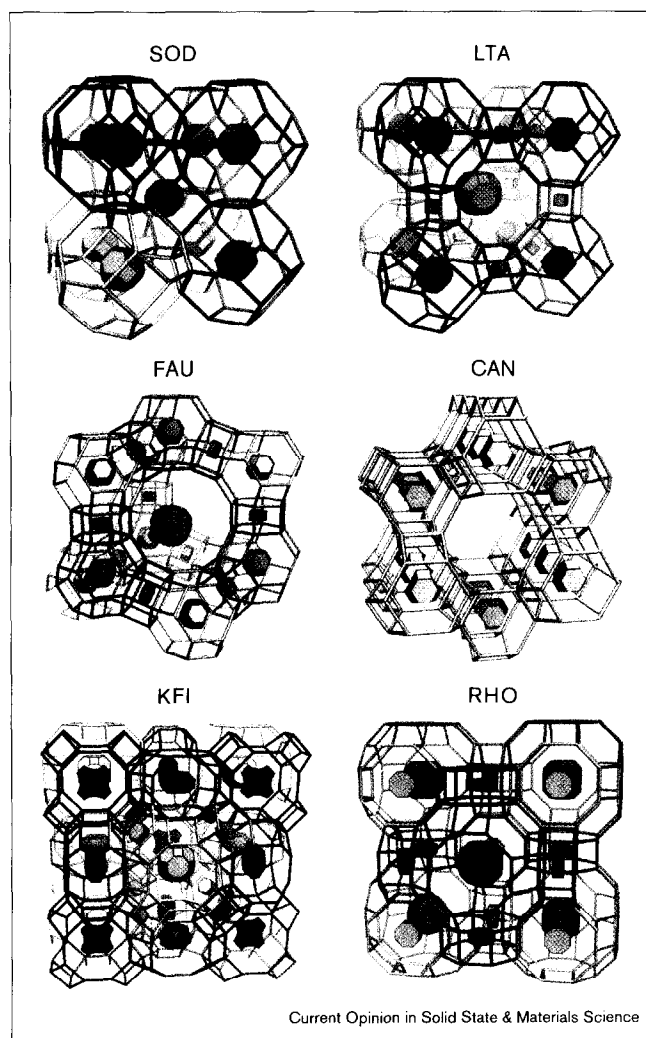
This review is concerned with crystalline molecular sieves, a class of porous crystalline open-framework solids which includes aluminosilicates (zeolites), aluminophosphates and related materials [2–4]. Zeolites are built from corner-sharing  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra linked by the apical oxygen atoms to form frameworks of high internal surface area with regular one-, two- or three-dimensional channel systems and cavities of molecular size (Figure 1). Other elements, such as Ga, Ge, B and Fe can substitute for Si and Al in the framework. The net negative charge of the framework, equal to the number of the constituent Al atoms, is balanced by exchangeable cations located in the channels which normally also contain water. The name 'zeolite' (from the Greek  $\zeta\epsilon\omega$  = to boil and  $\lambda\iota\theta\omicron\sigma$  = stone) was coined to describe the behaviour of the mineral stilbite which loses water on heating and thus seems to boil. There are  $\approx 40$  identified zeolite minerals and another 40 recognized synthetic species with a wide range of compositions. All known zeolites, both natural and synthetic, contain channels circumscribed by 12 or fewer tetrahedrally coordinated Si or Al atoms. Microporous silicates with windows of insufficient size to sorb water molecules reversibly are known as clathrasils [5].

The  $\text{AlPO}_4$  molecular sieves, the porous crystalline equivalents of aluminium phosphate, are built from alternating  $\text{AlO}_4$  and  $\text{PO}_4$  tetrahedra [6]. Incorporation of an Si source into  $\text{AlPO}_4$  gives silicoaluminophosphates, SAPO, and the incorporation of a metal (Me) into  $\text{AlPO}_4$  and SAPO gives the MeAPO and MeAPSO sieves, respectively. Other zeolite-related structures with novel compositions such as zincosilicates, gallophosphates, aluminarsenates, galloarsenates and beryllphosphates have also been reported [1]. Of the 43 recognized  $\text{AlPO}_4$  and related structures, 16 have the framework topologies of known zeolites, and the rest are novel structures (Table 1 and Figure 2). Unfortunately, although some microporous aluminophosphates contain wider channels than any known zeolite ( $> 1$  nm), their practical value is limited by their poor thermal stability. The structures of all known zeolitic,  $\text{AlPO}_4$  and related structures are listed in the 'Atlas of Zeolite Structure Types' by Meier, Olson and Baerlocher [1], while their topology and geometry have been extensively reviewed by Smith [7].

## Topological considerations

In the vast majority of molecular sieves Si, Al and P atoms (known as T-atoms) occupy 4-connected vertices of a three-dimensional net, and the O atoms occupy 2-connected positions between the 4-connected vertices. Thus each T-atom is surrounded by four oxygens and each oxygen by two T-atoms, which is written symbolically as (4;2). However, in some frameworks oxygen atoms are linked to

Figure 1



Framework structures of uninodal zeolites of structure types SOD (sodalite), LTA (zeolite A), FAU (faujasite), CAN (cancrinite), KFI (zeolite ZK-5) and RHO (zeolite Rho). The positions of tetrahedral atoms are at the crossings of the straight lines which symbolize T-T linkages. Oxygen atoms (not shown) lie approximately half-way between the T-atoms. The types of cages involved in each structure are represented by polyhedra which have been shrunk towards their centres. Sodalite (structure type SOD) is formed by direct face-sharing of four-membered rings in the neighbouring truncated octahedra, more correctly described as tetrakaidodecahedra (also known as 'sodalite cages' or ' $\beta$ -cages'). Zeolite A (structure type LTA) is formed by linking the sodalite cages through double four-membered rings. Faujasite (structure type FAU) is formed by linking the sodalite cages through double six-membered rings. Cancrinite is formed by direct linking of 11-hedra (' $\epsilon$ -cages' or 'cancrinite cages'). Other polyhedra are also present: the ' $\alpha$ -cage' (26-hedron of type I); double 8-membered ring; double 6-membered ring (hexagonal prism) and the 18-hedron (' $\gamma$ -cage'). Exchangeable nonframework cations are not shown for clarity.

one or three T-atoms; in others, T-atoms may be connected to 5 or 6 oxygens [8]. Given that each oxygen always lies between two T-atoms, the topology of the framework may be considered simply in terms of the connectivity of the T-atoms. Thus each T-atom is treated as a vertex of a

three-dimensional net, and each vertex lies at the intersection of four T-T edges. Such a net is said to be 4-connected. If all vertices in a net are topologically identical, the net is described as uninodal; binodal, trinodal and so on, nets are those with two, three and more topologically distinct types of vertices.

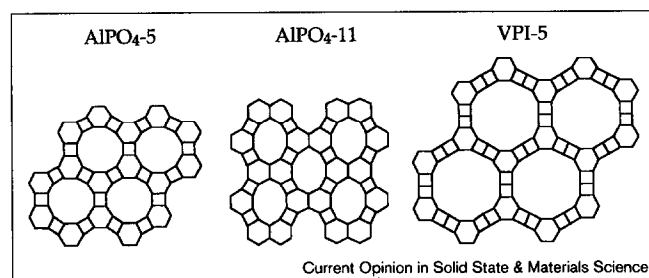
How are the different periodic nets described and classified? The diversity of known structures and the current state of mathematical knowledge are such that a topological classification of structures is necessarily based on common subunits of linked tetrahedra, known as secondary building units (SBUs) (Figure 3) [9]. The SBUs are the smallest number of simple units from which all known structures can be built. Some SBUs are thought to be precursor molecular fragments present in the synthesis gel from which the molecular sieve was crystallized. As new structures are discovered, new SBUs are added to the list.

Polyhedral cages, the larger building blocks, are each composed of a handful of SBUs and can in turn be combined to form an infinite framework. For example, the truncated octahedron (or  $\beta$ -cage), may be linked directly to other  $\beta$ -cages to form the SOD (sodalite) structure type, via double 4-membered rings to form zeolite A (LTA structure type), or via double 6-membered rings to form the zeolitic mineral faujasite (FAU) (Figure 3). Polyhedra are described by their face symbol: thus the sodalite cage is described as  $4^66^6$ , which specifies a polyhedron built from six 4-membered rings and six 6-membered rings. Alternatively, frameworks may be described in terms of chains of linked tetrahedra. Using a limited number of chains as building blocks, it is possible to generate molecular sieve structures in a similar way to that used to generate SBUs.

A periodic network of tetrahedral atoms can be described in terms of the 'circuit symbol' of each T vertex. Each T vertex participates in six  $T_i-T_j$  angles, and for each angle there is a shortest circuit of edges  $T-T_1 \dots T_j-T$ . The set of six numbers forms the circuit symbol of the vertex [10], which reflects the degree of compactness of a net. A simplified form of the circuit symbol is 'loop coordination': a graph showing only the number of 3- or 4-membered rings in which a given T-atom participates (see Figure 4).

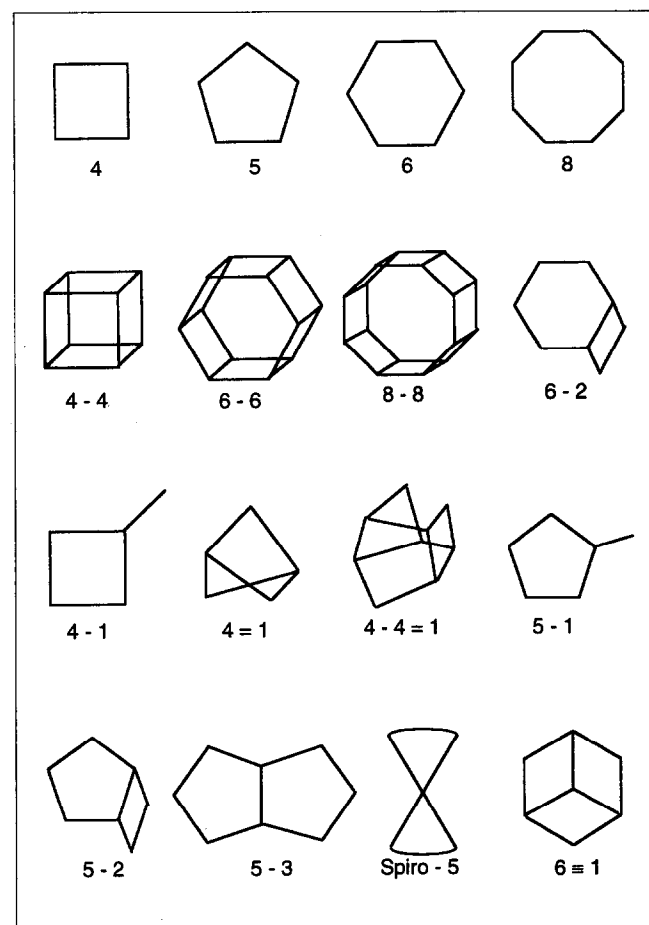
A very powerful description of a net involves the concept of a 'coordination sequence' (CS), originally introduced by Brunner and Laves [11] and first applied to molecular sieves by Meier and Moeck [12]. Thus in a 4-connected network each T-atom is connected to  $N_1 = 4$  neighbouring T-atoms through oxygen bridges. These are then linked to  $N_2$  T-atoms in the next shell, in turn connected to  $N_3$  T-atoms and so on, including each T-atom only once. For example, the coordination sequence for faujasite is: 4, 9, 16, 25, 37, 53, 73, 96, 120, 145. The coordination sequence satisfies the condition that  $N_0 = 1$ ,  $N_1 = 4$ ,  $N_2 \geq 12$ ,  $N_3 = 36$ ,  $N_k \leq 4 \cdot 3^{k-1}$  and is a periodic function [13]. Although the coordination sequence for each kind of T-atom is not

Figure 2



Framework projections of  $\text{AlPO}_4\text{-5}$  along [001],  $\text{AlPO}_4\text{-11}$  along [100] and VPI-5 along [001]. Neither of the three structures has a naturally-occurring analogue.

Figure 3



Secondary building units (SBUs) found in molecular sieve structures. The numbers indicate in how many known structure types a given SBU is found. Reproduced with permission from [1].

completely unique to a given structure, and occasionally distinct structures (such as LTA and RHO or ABW and ATN; see Table 1) have the same coordination sequence, it is a very useful guide because structures with different coordination sequences are guaranteed to be different. Framework density (FD) is defined as the number of

Table 1

### Microporous zeolitic and related molecular sieves.

Silicates				Silicates and phosphates		Phosphates
AFG	FER	MFI	RSN	ABW	AEI	ATV
*BEA	GME	MFS	RTE	AFI	AEL	AWW
BIK	GOO	MON	RTH	ANA	AET	CGF
BOG	HEU	MOR	RUT	AST	AFO	-CLO
BRE	IFR	MTN	SGT	BPH	AFR	CZP
CAS	JBW	MTT	STI	CAN	AFS	DFO
-CHI	KFI	MTW	TER	CHA	AFT	OSI
CON	LIO	MWW	THO	ERI	AFX	SAO
DAC	LOV	NAT	TON	FAU	AFY	VFI
DDR	LTL	NES	VET	GIS	AHT	WEI
DOH	LTN	NON	VNI	LAU	APC	ZON
EAB	MAZ	OFF	VSV	LEV	APD	
EDI	MEI	-PAR	WEI	LOS	ATN	
EMT	MEL	PAU	-WEN	LTA	ATO	
EPI	MEP	PHI		RHO	ATS	
EUO	MER	-RON		SOD	ATT	

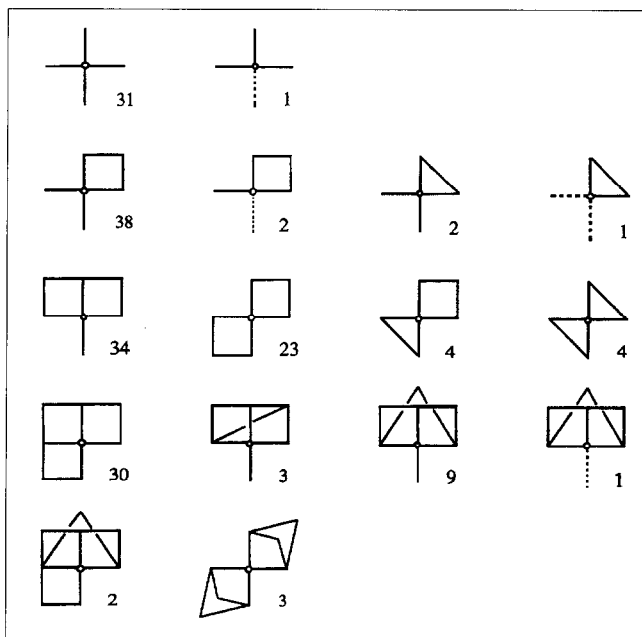
T-atoms per  $1000 \text{ \AA}^3$ , whereas topological density,  $\rho_{10}$ , is defined such that  $1000\rho_{10}$  is the number of T-atoms in the first ten coordination shells of a given T-atom [14,16] and also reflects the degree of compactness of a net.

The most recently introduced structural descriptions of molecular sieves use the concept of nodal surfaces [17] defined by wave vectors in a reciprocal space; equipotential surfaces, defined by point charges in real space, and triply periodic minimal surfaces (TPMS), that is surfaces with zero mean curvature at all points [18–20]. If a minimal surface has space group symmetry, it is periodic in three independent directions. Minimal surfaces have been shown to appear in a variety of real structures including cristobalite, diamond, quartz, ice and many molecular sieves. These concepts are fundamentally different from the 'conventional' approaches described above in that they do not consider chemical bonds and bond angles but treat structures as an assembly of atoms 'decorating' an infinite surface.

### Structural enumeration

In two dimensions, there are 11 different topological types of uninodal nets, a result already shown by Kepler [21]. Similarly, there are 508 and 16,774 types of binodal and trinodal nets, respectively. However, in three dimensions even the number of types of uninodal nets is infinite (although the number of 'realizable' ones may well be finite, see below). Finding interesting new nets therefore amounts to selecting a subset of an infinite set using certain criteria. The basic topological discussion of three-dimensional nets was given by Wells [10,22,23], who attached special importance to uniform nets in which the shortest rings at every angle are equal in length. Enumerations reported so far have been derived by empirical methods, and new structures were predicted by linking together structural subunits (SBUs, chains or cages) in new ways, either by building models or by computer sim-

Figure 4



Loop configurations and the number of structures in which they occur. Solid lines represent T-O-T linkages, dotted lines nonconnected T-O bonds found in interrupted frameworks. Reproduced with permission from [1].

ulation. As the T-O distances in all known zeolites are in the range 1.58–1.78 Å (such that all T-T edges are close to 3.1 Å) and the T-O-T angles in the range 130–160°, models of these can be built using identical sections of plastic tubing attached at each end to tetrahedral nodes.

However, of the many structures which are generated, only some will be 'chemically reasonable' [24]. Topology takes no account of chemistry and the basic requirement for chemically realistic structures is that bond lengths and angles are within a certain acceptable range. For example, one must reject hypothetical structures in which the distance between the vertices is smaller than the sum of atomic radii of the T-atoms involved. O'Keeffe [14] describes 'realizable' nets which can be realized geometrically with each vertex having only four equidistant nearest neighbours and with the T-T linkages corresponding to the edges of the net, and he believes that the number of such uninodal nets is not only finite, but amounts to 'some hundreds'. Given a realizable hypothetical structure, a least-squares fit leading to optimal T and O positions can then be performed by computer.

A very powerful criterion of realizability is the framework density. For the known zeolites and zeolite-type materials, FD values range from 12.5 to  $\approx$  20.5. Brunner and Meier [25] have shown that the range of the observed FD values in tetrahedral networks depends on the type and relative number of the smallest rings (Figure 5). The frameworks

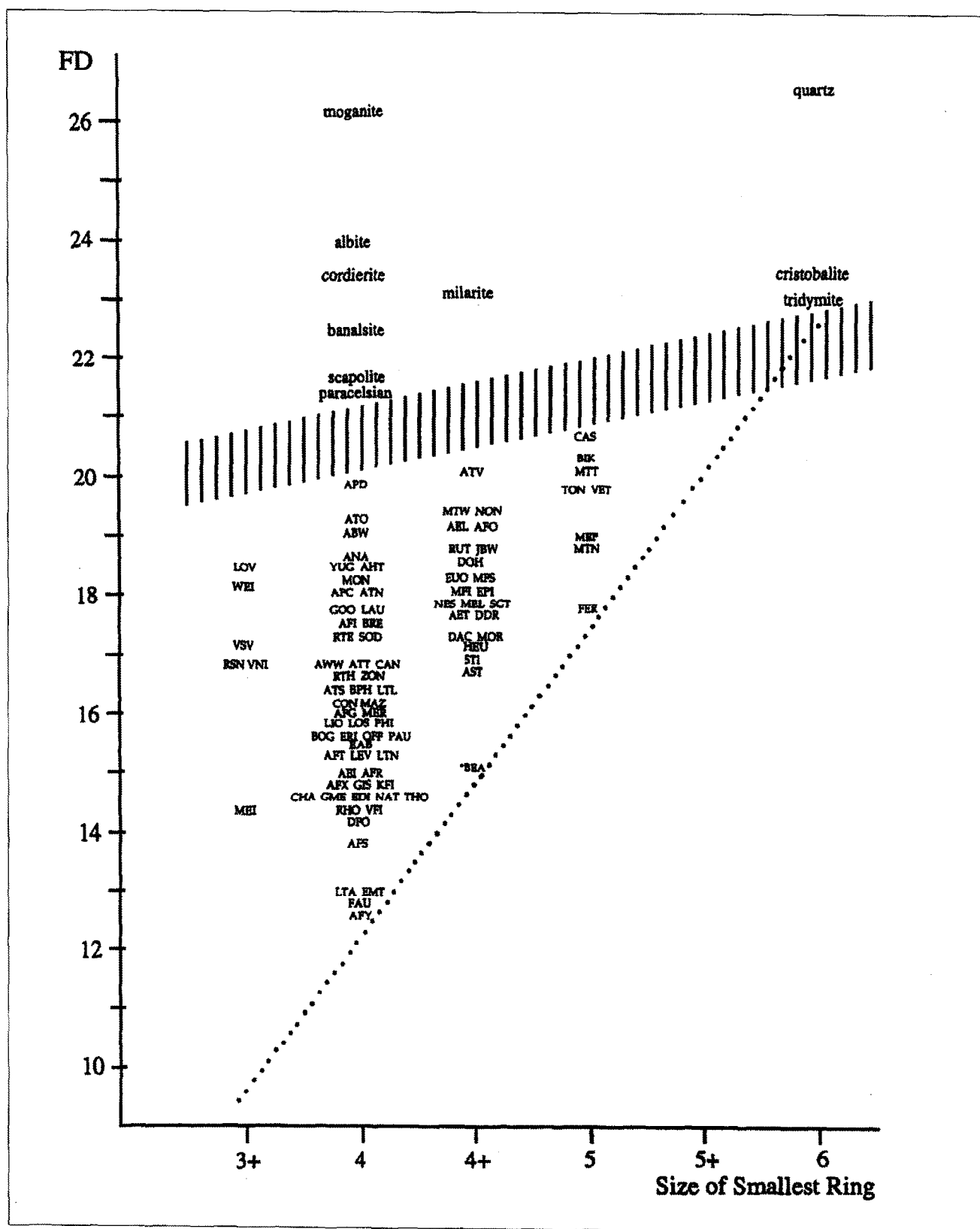
of lowest density have a maximum number of 4-membered rings, and the minimum framework density increases with the size of the smallest rings. They have demonstrated [25] that there is a clear gap in the FD values between zeolitic and dense frameworks and a lower limit to framework density, with the position of both dependent on the size of the smallest rings present in a given structure. These results have considerable predictive value for assessing the viability of hypothetical structures and can serve as a guide for the synthesis of low-density framework structures.

Brunner [26] addressed the question of the likelihood of preparing highly siliceous frameworks of a given topology, much in demand by industry, in terms of the loop configuration. In an article significantly entitled 'Quantitative zeolite topology can help to recognize erroneous structures and to plan syntheses' [27] he characterized open and dense tetrahedral structures with respect to the smallest rings, bond angles, symmetry, loop configuration and framework density. The conclusion was that the lowest density is obtained for structures of high symmetry. The largest cavities are usually found in the positions of highest symmetry of the space group, and two 4-rings with a common edge prefer the *cis* conformation, with nearly planar rings and a maximum of T-O-T angles near 109° over the *trans* conformation.

Aware of the practical importance of nets with very open frameworks (FD < 12) and wide channel openings (containing a maximum of 3- and 4-rings), Barrer and Villiger [28] were the first to find a chemically realistic net with unidimensional 18-ring channels, and Meier [29] and Hansen [30,31] derived a series of low-density nets. In a long sequence of papers, Smith and his coworkers have described a large number of hypothetical stereochemically realizable structures [32–46]. One of their most interesting results was the prediction [47] of the (4;2) net with 18-rings (described as net 81(1) in the original paper) which was subsequently identified in the aluminophosphate VPI-5 (VFI structure type) [48]. Using four different kinds of geometrical transformations, Andries and Bosmans [49] were able to enumerate, systematically, (4;2)-connected 3D nets related to the (nonzeolitic) tridymite group.

O'Keeffe *et al.* [14–16,50–55] have derived many new structures using empirical computer search algorithms. A point was moved in small increments throughout the asymmetric unit of the unit cell of all the cubic, hexagonal, tetragonal and orthorhombic space groups in turn. All the equivalent points in the cell, generated by the group-symmetry operations, were then identified. The topology of the net defined by the four nearest neighbours of the initial point was then characterized by its coordination sequence. In this way, O'Keeffe was able to describe and characterize topologically, 11 uninodal nets in which the shortest rings containing each pair of edges are N-rings (N > 4) and 13 nets without 3- or 4-rings [14], 19 uninodal nets containing 3-rings [15] and 21 nets in which at least

Figure 5



Distribution of framework densities versus the smallest ring in the network. The hatched region represents the gap between dense and microporous framework types [25], and the dotted line marks the lower limit for the framework density. The '+' sign next to a ring size indicates that some T-sites are associated with larger rings than the one in question. Please refer to Table 1 for zeolite and microporous sieve type. Reproduced with permission from [1].

three of the shortest rings containing each pair of edges are 4-rings [54]. Most of these nets are new. He has also shown [16] that the coordination sequence for many simple 4-connected nets can be expressed by sets of quadratic equations, which can in some cases be reduced to a single equation. The coefficient of the quadratic term is related to the geometric density. O'Keeffe described low-density nets with a high proportion of three rings and showed that in terms of density correlations they form a group separate from typical zeolite nets.

Very recently, Treacy [56] described a computer method for generating periodic 4-connected frameworks. Given the number of unique tetrahedral atoms and the type of crystallographic space group, the algorithm systematically explores all combinations of connected atoms and crystallographic sites, seeking the 4-connected graphs. The resulting symmetry-encoded graphs are relaxed by simulated annealing and to identify the regular tetrahedral frameworks. Results were given for one unique tetrahedral atom in each of the 230 crystallographic space group types. Over 64,000 unique 3-dimensional and 4-connected uninodal graphs were found when the search was restricted to those topologies which connect to nearest-neighbour asymmetric units. In any given space group, the number of graphs can depend on the choice of asymmetric unit. About 3% of the 4-connected graphs refined to reasonable tetrahedral conformations, and many were described. The combinatorial explosion of graphs as the number of unique vertices is increased at present restricts this method to consideration of small numbers of unique atoms.

Hyde *et al.* [57,58] have shown that many low-density frameworks are related to periodic minimal surfaces of known surface area, thus providing a connection between FD and the average size of rings decorating the surface. Having considered the relation between density and bond lengths and angles, they gave upper and lower bounds of density as a function of the average ring size. The fact that the area per vertex on the surfaces is the same as that for related sheet silicates implies that framework density can be inferred from the average ring size alone. The lower bound for the density is consistent with the preferred bonding geometry of  $\text{SiO}_2$  networks. The results were considered in light of framework densities of highly siliceous zeolites, clathrasils and dense silicates in order to separate the roles of geometry and chemistry in determining framework topology. Using an analogy with three-connected networks of hyperbolically-curved single sheets, Fogden and Jacob [59] described a method for construction of frameworks corresponding to their interconnected, double-sheet relatives, and gave models of hypothetical frameworks fitting the triply-periodic minimal surfaces P, D and G. The channels and cavities in these structures are significantly larger than those in known zeolites.

Finally, it is important to mention that recent advances in mathematical tiling theory [60] are likely to lead to new

ways of systematic enumeration of a variety of chemical structures, including molecular sieves [61].

## Conclusions

Enumeration of networks of atoms in inorganic structures in general and in the commercially important microporous molecular sieves in particular is a highly desirable objective. Unfortunately, there is still no systematic procedure for such enumeration. As a result, all hypothetical structures reported so far were derived by empirical methods, and new structures were predicted by linking together structural subunits in new ways, either by building models or by computer simulation. A systematic and reliable enumeration procedure would not only reveal possible further structures, but could assist in the design of new synthetic routes by using suitable 'structure-directing' molecules. However, recent advances in tiling theory may lead to new ways of systematic enumeration of a variety of chemical structures.

## Acknowledgements

This paper is dedicated to Sir John Meurig Thomas (FRS) on the occasion of his 65th birthday. I am grateful to O Delgado Friedrichs, University of Bielefeld, for Figure 1.

## References

1. Meier WM, Olson DH, Baerlocher C: *Atlas of Zeolite Structure Types* (updates on <http://kristall.erdw.ethz.ch/IZA-SC/>), London: Elsevier; 1996.
2. Barrer RM: *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*. London: Academic Press; 1978.
3. Breck, DW: *Zeolite Molecular Sieves: Structure, Chemistry and Use*. London: John Wiley; 1974.
4. Szostak R: *Molecular Sieves: Principles of Synthesis and Identification*. New York: Van Nostrand Reinhold; 1989.
5. Liebau F, Gies H, Gunawardane RP, Marler B: **Classification of tectosilicates and systematic nomenclature of clathrate type tectosilicates: a proposal**. *Zeolites* 1986, **6**:373-377.
6. Wilson ST, Lok BM, Messina CA, Cannan TR, Flanigen EM: **Aluminophosphate molecular sieves: a new class of microporous crystalline inorganic solids**. *J Am Chem Soc* 1982, **104**:1146-1147.
7. Smith JV: **Topochemistry of zeolites and related materials. 1. Topology and geometry**. *Chem Rev* 1988, **88**:149-182.
8. Liebau F: *Structural Chemistry of Silicates. Structure, Bonding, and Classification*. Berlin: Springer; 1985.
9. Meier WM: **Zeolite structures**. In *Proceedings of the 1st International Zeolite Conference: 1967 April 4-6; London*. Edited by Barrer RM: Society of Chemical Industry; 1968.
10. Wells AF: *Further Studies of Three-Dimensional Nets, American Crystallographic Association Monograph No. 8*. Pittsburgh: Polycrystal Book Service; 1979.
11. Brunner GO, Laves F: **Zum Problem der Koordinationszahl**. *Wiss Z Tech Univ Dresden* 1971, **20**:387-390. [Title translation: On the problem of coordination number.]
12. Meier WM, Moeck HJ: **The topology of three-dimensional 4-connected nets: classification of zeolite framework types using coordination sequences**. *J Solid State Chem* 1979, **27**:349-355.
13. Grosse-Kunstleve RW, Brunner GO, Sloane NJA: **Algebraic description of coordination sequences and exact topological densities for zeolites**. *Acta Cryst A* 1996, **52**:879-889.
14. O'Keeffe M, Brese NE: **Uninodal 4-connected 3D nets. I. Nets without 3-rings or 4-rings**. *Acta Cryst A* 1992, **48**:663-669.

15. O'Keeffe M: **Uninodal 4-connected 3D nets. II. Nets with 3-rings.** *Acta Cryst A* 1992, **48**:670-673.
16. O'Keeffe M, Hyde ST: **The asymptotic behavior of coordination sequences for the 4-connected nets of zeolites and related structures.** *Z Krist* 1996, **211**:73-78.
17. Brenner S, McCusker LB, Baerlocher C: **Using periodic nodal surfaces to facilitate structure solution from powder diffraction data.** *Appl Cryst* 1997, in press.
18. Andersson S, Hyde ST, von Schnering HG: **The intrinsic curvature of solids.** *Z Krist* 1984, **168**:1-17.
19. Andersson S, Hyde ST, Larsson K, Lidin S: **Minimal surfaces and structures - from inorganic and metal crystals to cell membranes and bio-polymers.** *Chem Rev* 1988, **88**:221-242.
20. Mackay AL: **Crystallographic surfaces.** *Proc Royal Soc Lond A* 1993, **442**:47-59.
21. Kepler J: *Harmonices Mundi Libri V, Book II, Sections 18-20.* Linz: 1619:51-56.
22. Wells AF: *Three-Dimensional Nets and Polyhedra.* New York: Wiley; 1977.
23. Wells AF: *Structural Inorganic Chemistry.* Oxford: Oxford University Press; 1984.
24. Gramlich-Meier R, Meier WM: **Constituent units and framework conformations in zeolite networks.** *J Solid State Chem* 1982, **44**:41-49.
25. Brunner GO, Meier WM: **Framework density distribution of zeolite-type tetrahedral nets.** *Nature* 1989, **337**:146-147.
26. Brunner GO: **Which frameworks will form SiO<sub>2</sub> analogs - the significance of loop configurations.** *Zeolites* 1993, **13**:592-593.
27. Brunner GO: **Quantitative zeolite topology can help to recognize erroneous structures and to plan syntheses.** *Zeolites* 1993, **13**:88-91.
28. Barrer RM, Villiger H: **The crystal structure of the synthetic zeolite L.** *Z Krist* 1969, **128**:352-370.
29. Meier WM: **Zeolites and zeolite-like materials.** *Pure Appl Chem* 1986, **58**:1323-1328.
30. Hansen S: **A series of hypothetical building units generating open zeolite-type nets.** *Naturwissenschaften* 1990, **77**:581-584.
31. Hansen S: **Expanding zeolite-type nets.** *Nature* 1990, **346**:799-800.
32. Smith JV: **Enumeration of 4-connected 3-dimensional nets and classification of framework silicates. I. Perpendicular linkage from simple hexagonal set.** *Am Miner* 1977, **62**:703-709.
33. Smith JV: **Enumeration of 4-connected 3-dimensional nets and classification of framework silicates. II. Perpendicular and near-perpendicular linkages from 4.8<sup>2</sup>, 3.12<sup>2</sup> and 4.6.12 nets.** *Am Mineral* 1978, **63**:960-969.
34. Smith JV: **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.** *Am Mineral* 1979, **64**:551-562.
35. Smith JV, Bennett JM: **Enumeration of 4-connected 3-dimensional nets and classification of framework silicates: the infinite set of ABC-6 nets; the Archimedean and s-related nets.** *Am Miner* 1981, **66**:777-788.
36. Smith JV: **Enumeration of 4-connected 3-dimensional nets and classification of framework silicates: Combination of 4-1 chain and 2D nets.** *Z Krist* 1983, **165**:191-198.
37. Smith JV, Bennett JM: **Enumeration of 4-connected 3-dimensional nets and classification of framework silicates: Linkages from the two (5<sup>2</sup>.8)2(5.8<sup>2</sup>)1 2D nets.** *Am Mineral* 1984, **69**:104-111.
38. Bennett JM, Smith JV: **Enumeration of 4-connected 3-dimensional nets and classification of framework silicates. 3D nets based on the 4.6.12 and (4.6.10)4 (6.6.10): 2D nets.** *Z Krist* 1985, **171**:65-68.
39. Smith JV, Dytrych WJ: **Enumeration of 4-connected 3-dimensional nets and classification of framework silicates. 3D nets based on double-bifurcated chains and the 4.8<sup>2</sup> and 4.6.12 3-connected plane nets.** *Z Krist* 1986, **175**:31-36.
40. Hawthorne FC, Smith JV: **Enumeration of 4-connected 3-dimensional nets and classification of framework silicates - body-centered cubic nets based on the rhombicuboctahedron.** *Can Miner* 1986, **24**:643-648.
41. Hawthorne FC, Smith JV: **Enumeration of 4-connected 3-dimensional nets and classification of framework silicates. 3D nets based on insertion of 2-connected vertices into 3-connected plane nets.** *Z Krist* 1986, **175**:15-30.
42. Hawthorne FC, Smith JV: **Enumeration of 4-connected 3-dimensional nets and classification of framework silicates. Combination of zigzag and saw chains with 6<sup>3</sup>, 3.12<sup>2</sup>, 4.8<sup>2</sup>, 4.6.12 and (5<sup>2</sup>.8)2(5.8<sup>2</sup>)1 nets.** *Z Krist* 1988, **183**:213-231.
43. Richardson JW, Smith JV, Pluth JJ: **Theoretical nets with 18-ring channels: enumeration, geometrical modeling, and neutron diffraction study of AlPO<sub>4</sub>-54.** *J Phys Chem* 1989, **93**:8212-8219.
44. Han SX, Smith JV: **Four-connected three-dimensional nets generated from the 1,3-stellated cube: topological analysis and distance-least-squares refinement.** *Acta Cryst A* 1994, **50**:302-307.
45. Andries KJ, Smith JV: **(4;2)-Connected three-dimensional nets related to the mixed-coordinated framework structures AlPO<sub>4</sub>-15, AlPO<sub>4</sub>-CJ2 and AlPO<sub>4</sub>-12.** *Acta Cryst A* 1994, **50**:317-325.
46. Andries KJ, Smith JV: **Opening, stellation and handle replacement of edges of the cube, tetrahedron and hexagonal prism. Application to 3-connected 3-dimensional polyhedra and (2,3)-connected polyhedral units in 3-dimensional nets.** *Proc Royal Soc Lond A* 1994, **444**:217-238.
47. Smith JV, Dytrych WJ: **Nets with channels of unlimited diameter.** *Nature* 1984, **309**:607-608.
48. Davis ME, Saldarriaga C, Montes C, Garces J, Crowder C: **A molecular sieve with 18-membered rings.** *Nature* 1988, **331**:698-699.
49. Andries KJ, Bosmans HJ: **The systematic enumeration of (4;2)-connected 3D nets related to the tridymite group.** *Acta Cryst A* 1990, **46**:847-855.
50. O'Keeffe M: **Dense and rare four-connected nets.** *Z Krist* 1991, **196**:21-37.
51. O'Keeffe M: **N-dimensional diamond, sodalite and rare sphere packings.** *Acta Cryst A* 1991, **47**:748-753.
52. O'Keeffe M: **Topological and geometrical characterization of sites in silicon carbide polytypes.** *Chem Mater* 1991, **3**:332-335.
53. O'Keeffe M: **Coordination sequences for lattices.** *Z Krist* 1995, **210**:905-908.
54. O'Keeffe M: **Uninodal 4-connected 3D nets. III. Nets with three or four 4-rings at a vertex.** *Acta Cryst A* 1995, **51**:916-920.
55. O'Keeffe M, Hyde BG: **Crystal structures I: patterns and symmetry.** In *Mineralogical Association of America Monograph*; 1996.
56. Treacy MMJ, Randall KH, Rao S, Perry JA, Chadi DJ: **Enumeration of periodic tetrahedral frameworks.** *Z Krist* 1997, **212**:768-791.
57. Hyde ST, Ninham BW, Blum Z: **The density of silicon-rich zeolite frameworks.** *Acta Cryst A* 1993, **49**:586-589.
58. Hyde ST: **The density of three-dimensional nets.** *Acta Cryst A* 1994, **50**:753-759.
59. Fogden A, Jacob M: **Hypothetical zeolite frameworks of ultra-low density.** *Z Krist* 1995, **210**:398-406.
60. Huson DH: **The generation and classification of tile-k-transitive tilings of the Euclidean plane, the sphere and the hyperbolic plane.** *Geometriae Dedicata* 1993, **47**:269-296.
61. Delgado Friedrichs O, Huson DH: **Tiling space by platonic solids.** In *Discrete and Computational Geometry* 1998, in press.