

Chemically feasible hypothetical crystalline networks

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Our systematic enumeration¹ of 4-connected crystalline networks (that is, networks in which each atom is connected to exactly four neighbours) used recent advances in tiling theory² to evolve over 900 topologies. The results are relevant to the structures of zeolites and other silicates, aluminophosphates (AlPOs), oxides, nitrides, chalcogenides, halides, carbon networks, and even to polyhedral bubbles in foams. Given their importance as molecular sieves, ion exchangers, catalysts and catalyst supports, we have applied the results to microporous aluminosilicates and aluminophosphates (zeolites). Zeolite chemistry has to date produced 152 distinct types of structure. However, it was always clear that although many further structures can be synthesised, only a fraction of the mathematically generated networks would be chemically feasible (many are 'strained' frameworks requiring unrealistic bond lengths and bond angles), and that an effective 'filtering' process is needed to identify the most plausible frameworks. Here, we describe the use of computational chemistry methods to calculate optimized structural parameters, framework energies relative to α -quartz, volumes accessible to sorption, and X-ray diffraction patterns for systematically enumerated hypothetical 4-connected crystalline frameworks. Structures were treated as silica polymorphs with the empirical formula SiO_2 , and their energies were minimized.

The problem is important as the results will assist in the design of synthetic routes that lead to novel materials. A database of X-ray diffraction patterns calculated for the hypothetical structures will be of great value for determining the structures of newly synthesised materials, as has already occurred when the VFI structure type was predicted³ and then found in the aluminophosphate VPI-5.⁴

Systematic enumeration identified networks with one, two and three kinds of inequivalent vertices, which we call uninodal, binodal and trinodal¹. We refer to the individual networks as n_{xx} , where n signifies the number of vertices, and xx is the (arbitrary) number of the net. Known structures were identified using the concept of the 'coordination sequence', which reflects the extent of branching in the net^{5,6}. Although the coordination sequence does not uniquely identify a given structure, different sequences must necessarily correspond to different structures. Some enumerated hypothetical networks correspond to well-known non-zeolitic minerals, and many are

duplicates (which were removed), leaving only 166, 113 and 624 unique uninodal, binodal and trinodal networks, respectively. As most of the uninodal networks, which include all 21 known uninodal zeolites, have already been enumerated^{1,7-10} and energetically evaluated¹¹, they will not be considered here. However, we believe that most of the binodal and trinodal networks are completely new, and many have very interesting structural features. Given the absence of an accessible collection of hypothetical structures and of a reliable method for the unique identification of topology, it is difficult to judge how many binodal and trinodal hypothetical networks have been generated before. In any case, their chemical feasibility has not been assessed. We hope that the topological identifier SYSTRE (Symmetry Structure Recognition), which unambiguously distinguishes different nets¹², will soon enable us to cross-reference structures derived using the various enumeration methods.

Advances in computer technology allowed us to use computational chemistry methods to calculate the unit cell parameters, framework energies (E_f), framework densities (F_D , defined as the number of tetrahedral atoms per $1,000 \text{ \AA}^3$), volumes available to sorption and X-ray diffraction patterns for the hypothetical frameworks treated as silica polymorphs with the empirical formula SiO_2 . Silicon atoms were inserted at each vertex of the enumerated networks, and a bridging oxygen atom was placed between each pair of neighbouring Si atoms. Each net was then scaled so that the vertices were separated by a typical Si-Si distance of approximately 3.1 \AA , and pre-optimized using the method of distance least squares¹³, which fits bond lengths and angles to the prescribed values. The energy minimization GULP program¹⁴ was used with the Sanders-Catlow silica potential¹⁵ and the modified oxygen shell charge given by Schröder¹⁶. The interatomic potential methods are fast, reliable and effectively reproduce known structures¹⁷, giving values for the lattice enthalpy that follow trends found experimentally^{18,19}. The Cerius² software suite (version 4.0, Molecular Simulations, San Diego) was used to calculate volumes available to sorption, space group symmetry (highest symmetry was also assumed) and other relevant parameters. Finally, framework energies were calculated relative to α -quartz, the most stable form of the mineral at ambient temperature. Relative framework energies and other relevant structural parameters were then compared with the corresponding

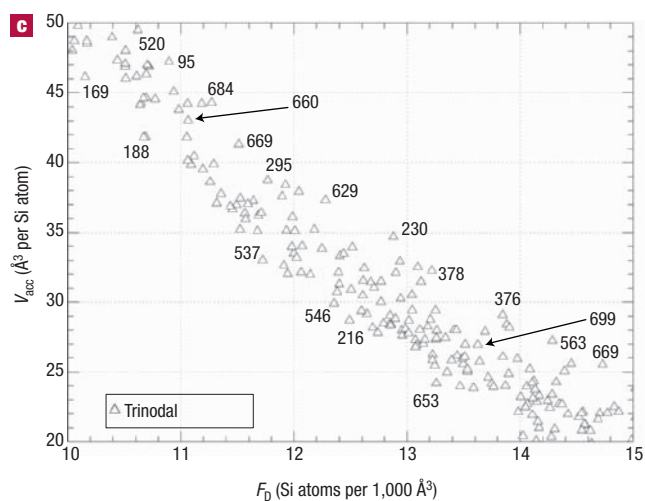
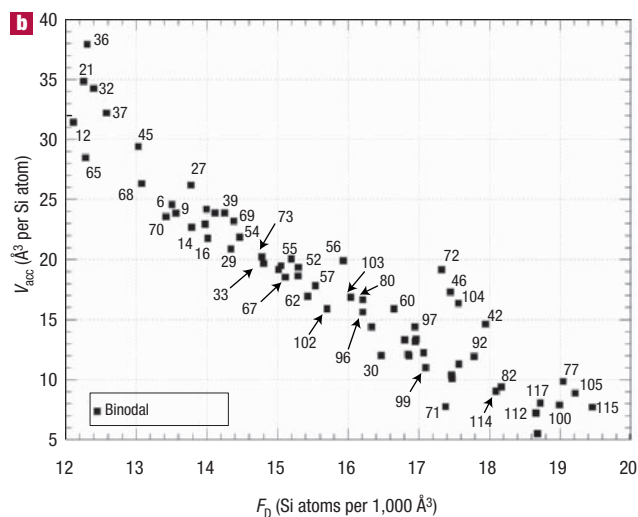
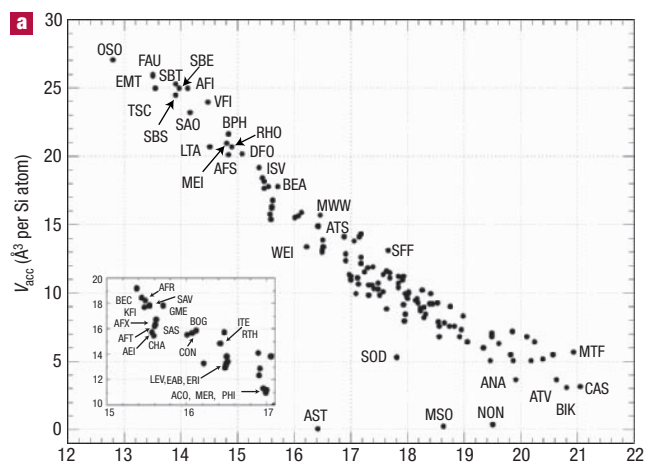
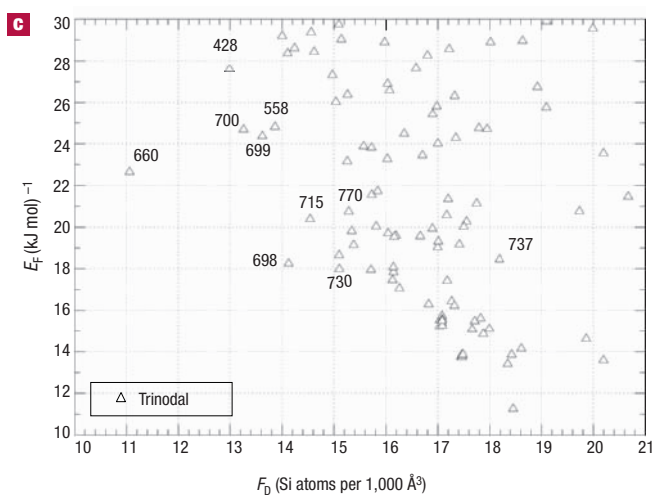
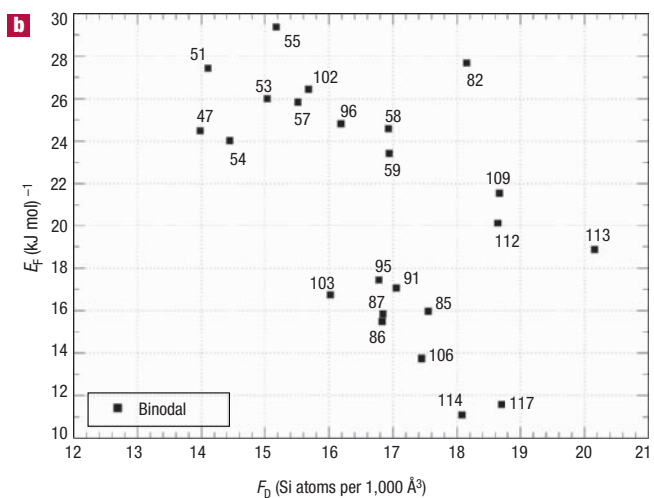
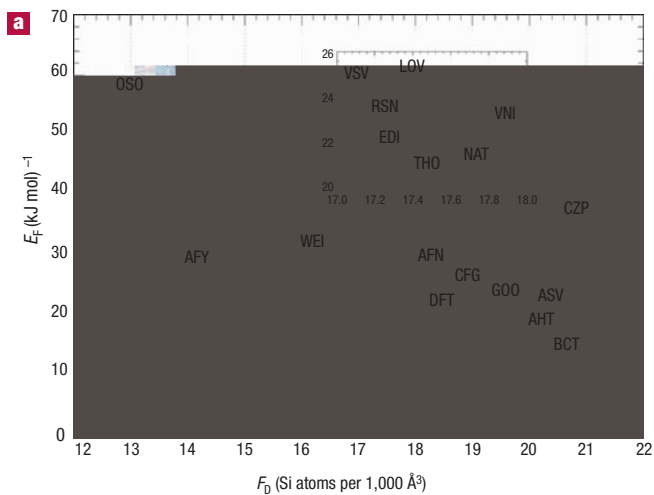


Figure 1 Framework energy with respect to α -quartz versus framework density. Data for **a**, all known zeolitic structure types treated as silica polymorphs, **b**, binodal and **c**, trinodal hypothetical structures with framework energies below 30 kJ mol^{-1} . Inset is an expansion of the plot to clarify the data points above AFN.

Figure 2 Accessible volume versus framework density. Data for **a**, all known zeolitic structure types treated as silica polymorphs, **b**, binodal and **c**, trinodal hypothetical structures.

values for known zeolite frameworks, also treated as silica polymorphs. A total of $164 + 111 + 612 = 887$ uninodal, binodal and trinodal structures were successfully optimized and ‘ranked’ according to their framework energies and available volumes, to give a subset of chemically feasible hypothetical structures.

Figure 1a gives the relative framework energies of all known zeolites treated as silica polymorphs (but excluding structure types –CHI, –CLO, –PAR, –RON and –WEN, which have interrupted frameworks) versus their density. The three structure types with energies that significantly deviate from the rest are WEI (a beryllophosphate), CZP (a zincophosphate) and OSO (a berylosilicate). The frameworks of OSO and WEI contain three-membered rings, and the higher energy of their siliceous forms indicates a strained framework. The relative lattice energies of the remaining zeolites correlate well with measured heats of transformation^{20,21}.

Figure 1b,c shows plots of the relative framework energy versus the framework density for the hypothetical binodal and trinodal frameworks with energies below 30 kJ mol^{-1} , the range considered as the most ‘desirable’ and with framework densities typical of the known zeolites. Prefixes 2_ and 3_ have been omitted for clarity.

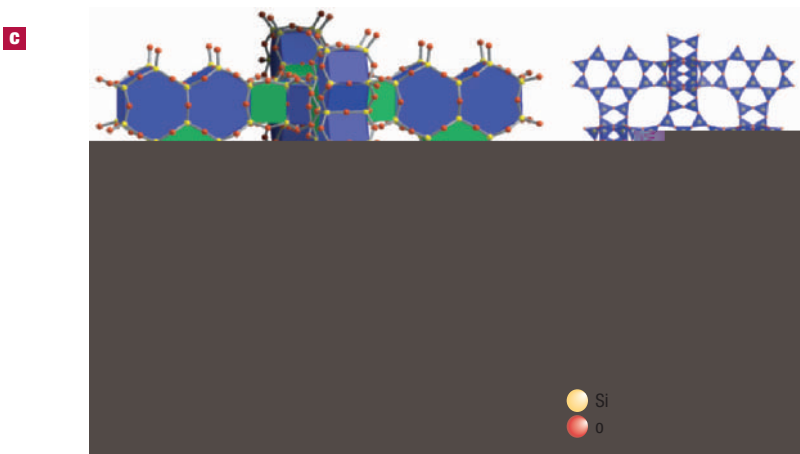
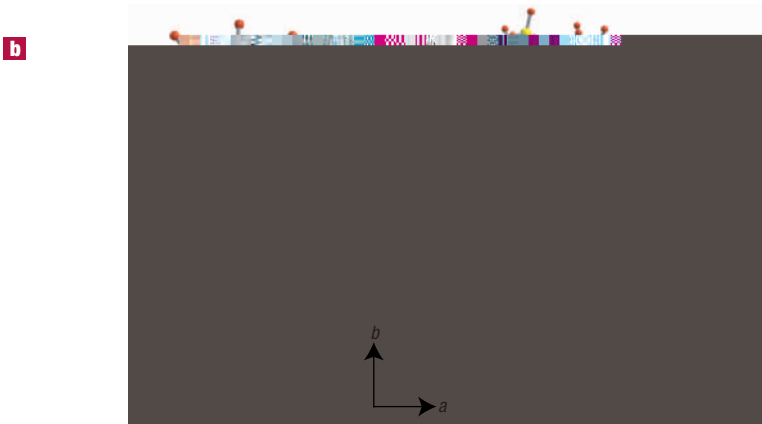
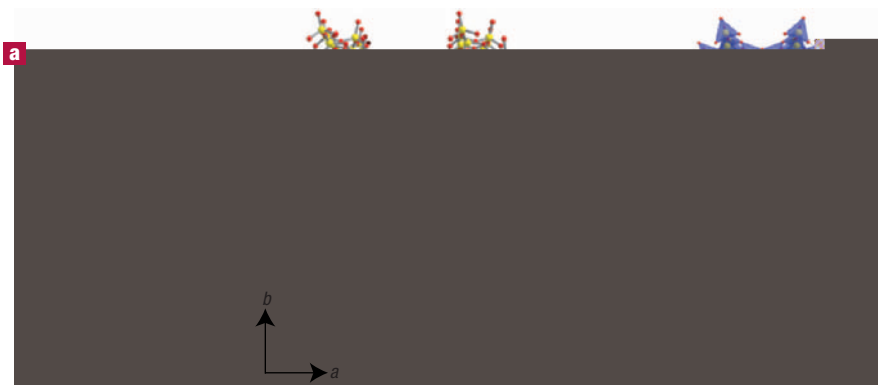
The space available for molecular sorption is an important consideration in zeolite chemistry. The Free Volume module of the Cerius² package, which applies the Connolly method²², was used to

calculate the ‘accessible volume’ of each structure (V_{acc} , defined as the volume that a probe molecule of a given radius delineates as it is ‘rolled over’ the van der Waals surface of the framework atoms, and which can be reached from the outside of the crystal): a probe molecule with 1.4 \AA radius (such as water), and 1.32 and 0.9 \AA for the van der Waals radii of O and Si atoms, respectively, were used for the calculations. Structures with low F_D are of particular interest, as they have high accessible free volumes. Figure 2a shows that the OSO, FAU, EMT and SBT frameworks have the highest accessible volumes. However, as many known structures (such as SOD, AST, MSO and NON) have dense frameworks, it was evident that hypothetical structures cannot be ruled out as chemically plausible just on the basis of low free accessible volume (although such structures will not be of interest for sorption, ion exchange or catalysis). Figure 2b,c shows plots of the accessible volume versus the framework density for the hypothetical binodal and trinodal structures.

Structures of the greatest practical interest are those with both low energies and large accessible volumes, and Fig. 3 plots the framework energy with respect to α -quartz for all hypothetical bi- and trinodal zeolitic structures versus the accessible volume, thus distilling the information in Figs 1 and 2.

A plot of framework density, F_D , for known zeolites and for dense silicate frameworks against the size of the smallest ring in the structure²³, shows that very open frameworks with low F_D have many 4- and 3-membered rings, and that there is a clear gap in F_D between compact minerals, such as quartz and tridymite, and the zeolite frameworks. The upper boundary of F_D for known zeolites is from about 19 tetrahedral atoms per $1,000 \text{ \AA}^3$ in materials with 3-membered rings to over 21 tetrahedral atoms in materials with 6-membered rings.

In conclusion, we were able to identify 25 and 107 feasible binodal and trinodal frameworks. However, some of them have low accessible volumes and are thus of limited practical interest. Figure 4a–d shows



similarity of the atomic radii of silicon and aluminium, but separate calculations would have to be made for materials with other chemical compositions.

Our tiling methods can be readily extended not only to 6-coordinated and mixed 6-/4-coordinated structures, but to any arbitrarily prescribed coordination. For 6-coordinated structures, we would start with a list of 6-faced generalized polyhedra instead of the tetrahedra we have used so far¹, and the number of resulting structures would be much larger than that considered here. The advantages of the tiling method of enumeration as compared with other approaches, is that it is systematic, and that certain aspects of the enumerated topologies, such as ring size and cage topology, can be prescribed in advance.

Many microporous materials are synthesised using templates (organic bases incorporated in the reactive mixture) that direct the shape of the resulting framework. A given framework may then be targeted by a suitable choice of the template using ZEBEDDE, a computational method for designing template molecules that are 'grown' within the target inorganic framework²⁶. ZEBEDDE is now being used to assist in the synthesis of the zeolitic structures that we have identified as chemically plausible.

Our results will have a considerable impact in the design of new synthetic routes and in the identification of the structures of newly synthesised materials. We note that two zeolite-like materials with the topologies of our hypothetical networks have recently been reported^{27,28}.

Structural information on all optimized structures, as well as crystallographic CIF files and simulated powder X-ray diffractograms for the structures discussed here, is given in the Supplementary Information. Complete structural information on all the enumerated structures is being placed on a website (<http://www.klinowski.ch.cam.ac.uk>).

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Supplementary Information accompanies the paper on www.nature.com/naturematerials

Competing financial interests

The authors declare that they have no competing financial interests.