

# Hypothetical binodal zeolitic frameworks

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Hypothetical binodal zeolitic structures (structures containing two kinds of tetrahedral sites) were systematically enumerated using tiling theory and characterized by computational chemistry methods. Each of the 109 refineable topologies based on ‘simple tilings’ was converted into a silica polymorph and its energy minimized using the *GULP* program with the Sanders–Catlow silica potential. Optimized structural parameters, framework energies relative to  $\alpha$ -quartz and volumes accessible to sorption have been calculated. Eleven of the 30 known binodal topologies listed in the Atlas of Zeolite Framework Types were found, leaving 98 topologies that were unknown previously. The chemical feasibility of each structure as a zeolite was evaluated by means of a feasibility factor derived from the correlation between lattice energy and framework density. Structures are divided into 15 families, based on common structural features. Many ‘feasible’ structures contain only small pores. Several very open structures were also enumerated, although they contain three-membered rings which are thermodynamically disfavoured and not found in conventional zeolites. We believe that such topologies may be realizable as framework materials, but with different elemental compositions to those normally associated with zeolites.

## 1. Introduction

Zeolites find many important applications in science and technology in areas as diverse as catalysis, chemical separation, water softening, agriculture, refrigeration and optoelectronics. There are 152 distinct structural types of zeolites which have now been identified (Baerlocher *et al.*, 2001). The definition of a zeolite is based not on chemical composition or function, but rather on atomic scale geometry. In order to qualify as a zeolite or zeolite-type material (zeotype), a mineral or synthetic material must possess a framework composed of corner-sharing tetrahedra. There is an additional requirement of ‘openness’, simultaneously dependent on density and smallest ring size, thus excluding denser minerals. Another way of expressing this is in terms of a four-connected net in which each vertex (in chemical terms the central atom of a tetrahedron) is connected to its four closest neighbours, normally *via* an oxygen bridge.

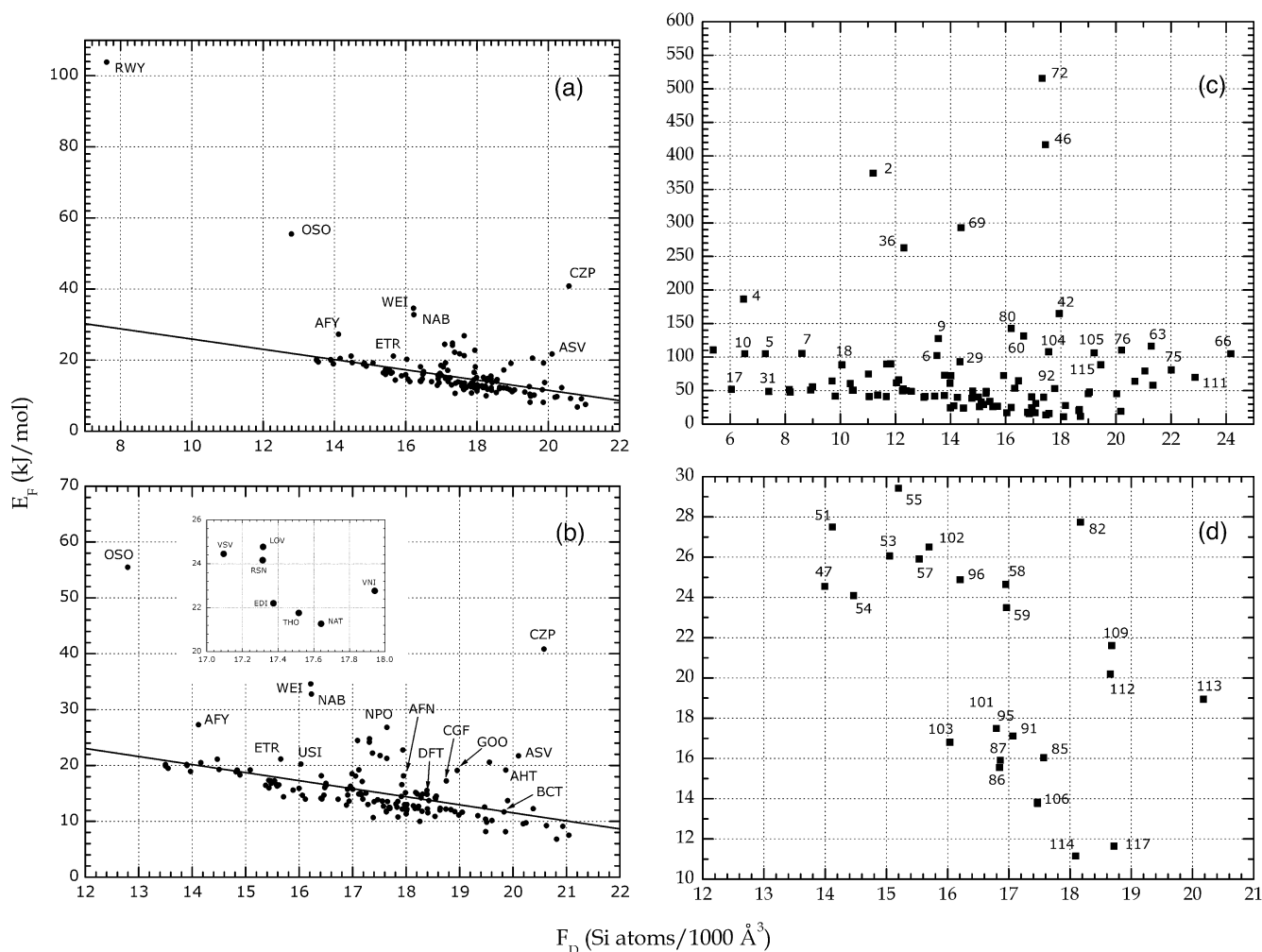
The enumeration of hypothetical zeolitic framework structures (Klinowski, 1998) is of considerable scientific and practical interest in terms of generating new nanoporous architectures. Enumeration originates with the work of Wells (1977, 1979, 1984) on three-dimensional nets and polyhedra. Smith and collaborators (Smith, 1988, 1993; Alberti, 1979; Sato, 1984, 1987; Sherman & Bennett, 1973; Barrer & Villiger, 1969), O’Keeffe and collaborators (O’Keeffe & Hyde,

1996*a,b*) and Akporiaye & Price (1989) found many possible new structures by combining various structural subunits. More recent work involves computer search algorithms (Boisen *et al.*, 1999; Treacy *et al.*, 1997; Foster & Treacy, 2004; Mellot-Draznieks *et al.*, 2000).

Our work is based on advances in combinatorial tiling theory (Dress *et al.*, 1993). A tiling is a periodic subdivision of three-dimensional space into connected regions, which we call *tiles*. If two tiles meet along a surface, the surface is called a *face*. If three or more faces meet along a curve, we call the curve an *edge*. If at least three edges meet at a point, we call that point a *vertex*. A network is thus formed by the vertices and edges. The configuration of edges, faces and tiles around a given vertex can be described *via* the so-called vertex figure, obtained by placing the centre of a small notational sphere at the vertex and considering the tiling of that sphere formed by the intersections with the different tiles touching that vertex. We have already enumerated all possible Euclidean uni-, bi- and trinodal tilings based on simple vertex figures and all uninodal tilings with vertex figures containing up to six extra

edges (Delgado Friedrichs, 2001), and the computer program used for this task is available from the authors upon request (olaf.delgado@asu.edu).

The tiling approach identified networks with one, two and three types of inequivalent vertices, which we call uninodal, binodal and trinodal (Delgado Friedrichs *et al.*, 1999). We have shown that there are exactly 9, 117 and over 1300 topological types of four-connected uninodal, binodal and trinodal nets, respectively, which are based on ‘simple’ periodic tilings (as explained in Delgado Friedrichs *et al.*, 1999). The previously reported number of 926 for the trinodal simple tilings included, due to an error in the manual processing of the data files, only those nets for which the tiles have non-trivial site symmetry. In addition, there are at least 157 additional uninodal nets derived from ‘quasi-simple’ tilings (the vertex figures of which are derived from tetrahedra, but contain double edges; Delgado Friedrichs *et al.*, 1999) and which have already been discussed elsewhere (Foster *et al.*, 2001, 2003; Foster, Friedrichs *et al.*, 2004; Foster, Simperler *et al.*, 2004; Simperler *et al.*, 2004;). For example, zeolitic structure types SOD, LTA,



**Figure 1** Framework energy,  $E_F$  (kJ mol<sup>-1</sup>), with respect to  $\alpha$ -quartz, versus framework density,  $F_D$  (Si atoms per 1000 Å<sup>3</sup>), for (a) and (b) all known zeolitic structure types; (c) and (d) hypothetical binodal zeolitic structures.

**Table 1**

Chemical feasibility factor, relative lattice energy, framework density and coordination sequences for 109 hypothetical binodal zeolites, optimized as purely siliceous structures.

Structures are listed in order of increasing value of  $\vartheta$ .

Structure	$\vartheta$	$\Delta E_{\text{quartz}}$ (kJ mol <sup>-1</sup> )	$F_D$ ( $T$ sites per 1000 Å <sup>3</sup> )	Coordination sequence
2_87	0.10	15.91	16.86	4 9 17 30 49 72 96 121 150 187
2_89 (ERI)	0.12	16.39	16.51	4 10 20 33 49 69 94 125 160 197
2_84 (EAB)	0.12	16.41	16.49	4 9 17 30 50 75 98 118 144 185
2_90 (SAT)	0.18	15.72	16.91	4 10 20 32 46 64 90 126 164 196
2_103	0.30	16.80	16.04	4 9 17 30 49 71 92 115 147 190
2_88 (AWW)	0.32	15.03	17.25	4 10 20 32 46 66 94 128 162 192
2_86	0.37	15.54	16.85	4 9 17 30 50 75 100 126 157 194
2_83 (LEV)	0.42	16.00	16.48	4 10 20 33 50 71 95 124 158 197
2_85	0.69	16.03	17.57	4 10 17 30 52 70 107 128 166 208
2_107 (LOS)	0.91	13.86	17.47	4 11 20 33 51 73 103 136 169 207
2_74 (TSC)	0.94	19.47	13.55	4 9 17 30 50 74 97 123 158 198
2_110	0.94	13.82	17.47	4 10 20 33 50 72 98 128 162 200
2_106	0.97	13.79	17.46	4 9 17 30 49 72 96 121 150 186
2_95	0.93	17.49	16.80	4 10 20 33 49 68 92 122 155 191
2_108	0.97	13.77	17.47	4 9 17 30 49 71 92 114 143 183
2_81 (SAS)	0.98	15.88	16.00	4 10 20 32 46 64 90 124 156 184
2_91	0.95	17.12	17.07	4 9 17 30 49 71 95 125 161 201
2_78 (AFX)	1.00	16.41	15.61	4 10 20 33 50 73 100 131 168 208
2_101 (AST)	0.99	18.14	16.41	4 10 20 34 52 74 102 136 172 210
2_117	1.22	11.58	18.74	4 9 16 25 37 53 74 99 125 151
2_114	2.17	11.15	18.09	4 9 17 28 41 56 73 93 117 146
2_47	3.02	24.55	14.00	4 10 20 34 53 76 103 135 170 209
2_54	3.18	24.09	14.47	4 9 18 32 52 75 99 133 171 207
2_112	4.66	20.19	18.66	4 10 19 32 52 76 103 136 172 213
2_50 (AFY)	5.03	27.27	14.12	4 9 17 29 45 64 85 110 141 178
2_53	5.11	26.05	15.05	4 9 17 29 45 65 89 116 144 175
2_51	5.18	27.49	14.12	4 9 19 34 48 66 96 127 151 183
2_59	5.25	23.49	16.96	4 12 18 28 52 78 88 112 162 204
2_113	5.32	18.94	20.19	4 11 24 41 64 93 127 163 205 255
2_96	5.45	24.88	16.21	4 12 22 44 64 94 124 164 206 252
2_57	5.51	25.91	15.54	4 11 21 36 64 93 120 156 202 255
2_109	5.67	21.61	18.68	4 11 23 40 62 88 123 162 202 249
2_58	6.04	24.64	16.95	4 9 17 28 41 56 74 97 125 158
				4 8 14 24 37 54 75 97 121 148
				4 8 14 25 40 57 76 96 119 150
				4 9 17 27 38 54 76 101 128 154
				4 10 22 40 60 95 121 165 212 258
				4 12 21 41 67 90 128 168 211 263
				4 8 14 25 39 53 71 96 124 152
				4 9 16 23 34 57 82 98 115 141
				4 7 12 24 39 60 79 110 168 250
				4 10 19 27 39 62 92 137 202 275
				4 8 14 25 39 53 72 100 130 157
				4 9 16 23 34 57 82 98 118 153
				4 9 18 32 52 75 99 133 171 207
				4 10 19 32 52 76 103 136 172 213
				4 10 23 38 60 86 118 154 195 244
				4 11 21 39 61 86 118 154 195 243
				4 9 18 32 52 75 105 144 181 217
				4 11 21 35 54 80 113 145 182 228
				4 8 14 26 44 63 80 97 122 164
				4 10 19 28 39 57 82 112 139 159
				4 10 20 34 53 76 102 133 170 212
				4 10 20 34 53 77 106 139 174 212
				4 8 14 26 45 67 89 115 149 188
				4 10 20 32 47 68 93 122 157 196

RHO, FAU, KFI and CHA are all based on quasi-simple tilings. An example of a non-simple tiling is that of GIS, where the tile has some two-connected vertices.

Here we focus our attention on the binodal structures, *i.e.* those with two topologically inequivalent types of tetrahedral vertex ( $T$ -atom sites) derived only from simple tilings, meaning that they can be readily described by the packing of convex polyhedra, the vertices of which are all three-connected. Structures containing cages are thus found in abundance, while those with, for instance, more 'cylindrical' channels are less common and tend to have lower framework density than the 'quasi-simple' structures, with a greater proportion lying in the range of density where most known zeolites are found, as opposed to denser minerals. On the other hand, many of the known zeolite structure types cannot be constructed from simple tilings. Thus, simple tilings cannot generate the complete set of binodal zeolites. Seven of the 21 known *uninodal* zeolites correspond to simple tilings, and the remaining 14, together with several mineral structures (although not quartz) are constructed using quasi-simple tilings. We have found 11 of the 30 known binodal zeolite types, and the remaining 19 will be found by considering quasi-simple tilings, just as with the uninodal structures. The number of potential binodal networks thus generated will be enormous, and their enumeration will require the use of state-of-the-art computational facilities. However, only very few binodal structures have previously been enumerated, while nearly all uninodal structures derived from the tilings were previously known, either as crystal structures or as hypothetical nets. It is therefore of interest to describe the binodal structures derived only from simple tilings.

To characterize the structures, we follow procedures identical to

Table 1 (continued)

Structure	$\vartheta$	$\Delta E_{\text{quartz}}$ (kJ mol <sup>-1</sup> )	$F_D$ ( $T$ sites per 1000 Å <sup>3</sup> )	Coordination sequence									
2_102	6.08	26.50	15.70	4 9 19 34 48 73 98 125 167 197									
				4 11 18 31 54 72 96 128 160 204									
2_55	7.61	29.43	15.20	4 8 14 26 44 62 91 121 144 181									
				4 11 19 29 47 67 91 121 153 188									
2_82	9.41	27.74	18.17	4 9 17 30 48 69 92 119 153 192									
				4 10 20 32 46 66 94 126 158 194									
2_67	10.27	33.41	15.11	4 8 16 28 42 60 84 108 136 170									
				4 9 16 27 43 62 83 109 139 171									
2_99	10.53	30.91	17.10	4 9 18 34 55 76 103 144 187 229									
				4 9 20 34 54 81 110 144 185 229									
2_35	10.69	41.65	9.82	4 8 13 20 28 36 46 62 83 104									
				4 9 15 21 28 37 49 65 85 108									
2_62	10.97	33.96	15.43	4 8 14 27 48 70 91 116 146 185									
				4 9 19 32 45 67 92 124 165 209									
2_43	11.62	41.22	11.05	4 8 14 21 34 53 71 90 108 133									
				4 8 16 27 35 48 66 83 113 146									
2_64	12.15	41.09	11.67	4 8 15 25 37 52 71 95 120 148									
				4 8 16 27 37 53 71 89 116 144									
2_45	12.91	40.22	13.03	4 8 14 23 34 49 67 87 111 139									
				4 9 16 25 37 52 70 91 114 140									
2_31	13.16	48.71	7.40	4 8 12 17 24 31 36 42 54 72									
				4 9 15 20 24 29 37 48 60 73									
2_24	13.28	43.16	11.36	4 7 12 22 32 41 56 80 106 125									
				4 9 15 22 32 46 63 81 100 122									
2_19	13.39	47.93	8.17	4 7 10 16 22 26 34 48 63 76									
				4 8 12 16 21 28 37 49 64 80									
2_73	13.62	38.71	14.78	4 9 15 21 37 59 104 138 182 199									
				4 11 20 36 52 77 121 155 192 236									
2_68	13.82	41.46	13.08	4 8 17 28 45 66 88 114 141 182									
				4 9 16 28 48 66 84 115 150 178									
2_39	13.86	39.83	14.25	4 8 13 22 36 53 72 94 122 156									
				4 9 16 25 38 56 78 103 129 157									
2_17	13.96	51.80	6.05	4 7 9 13 19 23 25 30 41 55									
				4 8 12 15 17 21 28 36 44 53									
2_70	14.33	41.70	13.42	4 8 17 32 46 71 95 129 166 199									
				4 9 18 32 50 70 95 128 166 212									
2_40	14.97	40.32	15.02	4 8 13 22 37 56 76 98 126 158									
				4 9 16 26 41 60 80 101 126 158									
2_27	15.42	42.76	13.78	4 7 12 24 38 50 68 94 122 153									
				4 9 16 26 40 57 78 103 130 159									
2_23	15.97	51.69	8.14	4 7 12 20 26 32 44 68 90 108									
				4 8 13 17 24 34 49 67 82 101									
2_20	16.11	50.76	8.93	4 7 10 17 27 35 41 52 73 100									
				4 9 15 20 25 33 47 66 84 98									
2_97	16.99	40.46	16.94	4 9 18 32 52 76 106 147 188 229									
				4 11 21 35 55 81 117 152 188 238									
2_71	17.07	39.95	17.38	4 8 19 39 58 83 118 160 193 232									
				4 10 21 38 58 91 117 158 195 244									
2_26	17.51	50.60	10.44	4 7 12 22 34 46 58 76 107 139									
				4 8 14 21 32 48 65 86 111 138									
2_25	17.56	50.63	10.47	4 7 12 22 33 44 58 80 104 125									
				4 8 14 21 32 48 65 85 106 132									
2_37	18.50	48.93	12.58	4 8 12 17 24 31 36 42 54 72									
				4 9 15 20 24 29 37 48 60 73									
2_21	18.85	49.90	12.26	4 7 10 18 32 47 59 71 91 121									
				4 9 16 24 34 48 66 89 117 149									
2_32	19.04	49.98	12.40	4 8 12 18 29 44 60 77 98 125									
				4 9 16 24 33 45 62 85 113 143									
2_48	19.09	45.87	15.29	4 8 14 25 38 50 70 100 125 147									
				4 9 16 24 36 56 76 92 120 159									
2_41	19.44	55.48	8.99	4 8 14 19 26 40 52 70 88 100									
				4 8 14 20 29 42 52 68 89 109									
2_69	20.57	49.50	14.25	4 8 17 29 46 68 91 117 154 184									
				4 9 17 28 49 69 92 119 151 184									
2_65	20.64	52.45	12.28	4 8 15 28 47 66 86 118 155 181									
				4 8 16 26 48 66 88 120 142 200									
2_33	20.83	49.10	14.80	4 8 12 18 30 49 71 92 114 143									
				4 9 16 25 38 56 77 99 121 147									
2_52	20.93	48.51	15.30	4 7 10 16 25 34 43 58 75 90									
				4 7 11 16 24 35 46 59 75 93									

those used in our previous work (Foster *et al.*, 2003; Foster, Simperler *et al.*, 2004). These involve generating model SiO<sub>2</sub> polymorphs from the tiling nets and optimizing them using lattice energy minimization. Apart from obtaining an optimized structure for each topology, we also calculate a lattice energy, which provides an accurate guide to the thermodynamic stability that such a phase might have. A ‘feasibility factor’,  $\vartheta$ , derived from the correlation between lattice energy and density calculated for known zeolite structure types, serves as a further measure of thermodynamic feasibility. We have also calculated the accessible volume for each pore system using a standard definition (Molecular Simulations Inc., 1999).

In describing the structural characteristics of each framework, we have resorted to the ‘model building’ approach (Baerlocher *et al.*, 2001; Smith, 1988; Meier, 1986; Liebau *et al.*, 1986), which is consistent with descriptions found in the online zeolite database and allows structures to be classified into ‘families’ if they share certain structural motifs. As part of this analysis we define as a composite building unit (CBU) every small finite unit from which a structure may be generated. These units can be corner-, edge- or face-sharing, or joined to one another by single linkages. The automated assembly of such units is also a potential method of structural enumeration, as demonstrated by Mellot-Draznieks (Mellot-Draznieks *et al.*, 2000, 2002). Zeolite structures may also be described in terms of the strictly defined secondary building units (SBUs), one type of which may be used to build a unit cell of the zeolite, without sharing  $T$  atoms. Here, we have not used the SBU approach, finding it more informative to use alternative descriptions (in general, our building units tend to be larger). However, the SBUs involved may be readily identified, as may the

Table 1 (continued)

Structure	$\vartheta$	$\Delta E_{\text{quartz}}$ (kJ mol <sup>-1</sup> )	$F_D$ (T sites per 1000 Å <sup>3</sup> )	Coordination sequence									
2_100	22.42	45.32	19.00	4 9 18 34 58 86 113 146 194 248									
				4 11 22 38 61 88 120 157 199 246									
2_79	23.48	45.37	20.03	4 9 17 29 46 69 98 133 174 221									
				4 10 21 37 58 84 114 148 186 229									
2_77	24.27	47.94	19.04	4 9 16 26 41 61 84 110 140 175									
				4 9 17 28 42 61 85 114 146 179									
2_44	24.31	60.53	10.36	4 8 14 21 36 55 75 94 120 154									
				4 8 16 20 34 64 72 96 128 146									
2_46	24.45	57.04	12.91	4 8 14 24 36 48 64 90 118 136									
				4 9 15 22 34 52 71 87 106 136									
2_61	25.45	53.55	16.33	4 8 14 26 46 70 91 113 149 197									
				4 10 19 30 45 68 94 122 152 186									
2_22	26.31	64.37	9.70	4 7 11 18 28 42 56 68 85 111									
				4 8 14 21 29 41 57 77 99 121									
2_92	26.57	53.08	17.78	4 9 17 31 54 82 109 139 182 233									
				4 11 22 35 55 82 110 146 188 230									
2_13	26.62	61.44	12.04	4 6 15 28 34 60 69 96 126 142									
				4 9 16 25 39 57 75 96 120 150									
2_93	28.25	60.99	13.98	4 10 20 31 50 71 104 134 176 210									
				4 9 18 30 48 70 94 134 180 213									
2_12	29.67	65.74	12.11	4 6 15 20 30 50 67 90 115 126									
				4 8 13 22 32 47 71 91 108 132									
2_30	33.21	64.55	16.47	4 8 12 16 26 42 56 72 102 140									
				4 8 13 20 30 41 56 80 111 138									
2_94	33.62	58.11	21.34	4 9 18 31 55 88 121 157 194 236									
				4 11 23 41 63 88 123 162 207 262									
2_16	36.19	72.38	14.02	4 6 17 32 49 65 92 135 167 183									
				4 11 20 28 50 81 102 117 159 222									
2_34	36.28	76.83	11.03	4 8 13 19 26 38 55 74 95 115									
				4 9 16 24 34 47 61 78 100 126									
2_14	36.36	72.96	13.79	4 6 16 31 48 57 77 116 154 161									
				4 11 19 26 42 70 93 103 128 182									
2_98	37.01	63.95	20.69	4 9 18 33 51 72 105 147 184 230									
				4 9 18 33 53 78 108 143 184 232									
2_56	38.29	72.66	15.93	4 8 14 26 44 62 93 122 145 182									
				4 11 19 29 47 68 94 123 155 193									
2_116	43.29	71.75	21.56	4 11 22 39 65 96 134 175 223 280									
				4 11 23 41 65 94 133 177 230 284									
2_111	43.36	69.96	22.87	4 10 20 46 70 94 140 206 264 308									
				4 12 25 47 74 108 155 203 262 334									
2_18	44.29	89.79	10.06	4 7 10 14 17 24 37 48 57 70									
				4 8 8 10 20 24 28 50 64 64									
2_28	45.34	88.96	11.69	4 7 13 18 33 44 66 72 110 118									
				4 8 12 21 30 50 58 82 98 138									
2_15	46.13	89.89	11.83	4 12 10 28 52 34 84 124 74 172									
				4 6 17 27 31 64 75 81 143 146									
2_75	50.08	80.91	22.01	4 7 13 25 39 56 87 107 148 182									
				4 8 14 25 40 59 84 110 147 180									
2_29	50.83	93.06	14.34	4 10 18 30 45 59 103 165 219 314									
				4 10 20 31 49 80 103 164 269 289									
2_10	51.21	104.88	6.53	4 6 12 16 24 32 44 55 68 80									
				4 6 12 17 24 31 44 55 68 82									
2_5	52.01	104.95	7.28	4 5 9 14 13 16 26 34 36 44									
				4 8 10 11 16 22 24 28 42 60									
2_115	52.70	88.37	19.46	4 11 21 36 64 94 123 165 214 272									
				4 11 23 40 63 91 126 167 213 265									
2_7	53.66	105.42	8.60	4 5 10 20 26 24 44 80 98 93									
				4 9 14 16 22 40 58 72 83 109									
2_8	54.06	110.45	5.39	4 6 7 12 19 21 22 30 46 58									
				4 8 12 13 16 22 30 36 44 56									
2_6	56.38	102.26	13.51	4 5 10 19 22 25 40 62 80 90									
				4 9 13 16 23 36 50 58 68 94									
2_104	64.22	107.73	17.56	4 10 17 30 52 72 108 130 167 208									
				4 11 20 33 52 76 105 138 173 213									
2_105	65.06	106.55	19.22	4 6 9 15 28 43 65 92 134 172									
				4 7 11 20 31 47 74 99 133 196									
2_76	68.64	110.29	20.21	4 9 16 25 38 58 87 124 165 209									
				4 10 20 34 53 78 109 146 191 245									
2_63	73.83	116.23	21.28	4 8 14 27 50 80 114 153 200 258									
				4 11 23 39 62 93 130 174 223 275									

infinite periodic building units (PerBUs). We note that none of the units discussed are intended to represent the precursors from which zeolite crystals grow; neither do they necessarily correspond to the tiles of the original nets.

We discuss the structures in terms of the component units, and relate these to the calculated stability and feasibility. Taken together, thermodynamic feasibility and the nature of the building units can provide a good initial guide as to which of these structures could be most readily synthesized.

## 2. Energy minimization

The systematically enumerated nets (Delgado Friedrichs *et al.*, 1999) were first converted into atomistic models. This was done by inserting an Si atom at each vertex point in the network and placing a bridging oxygen between each pair of adjacent Si atoms. Each net was scaled such that the vertices were separated by *ca* 3.1 Å, a typical Si—Si distance. The resulting structure was then pre-optimized using the DLS (distance least squares) method (Meier & Villiger, 1969), which performs geometric refinement of the structure by fitting bond lengths and angles to the prescribed values, and reduces the amount of computer time needed for the subsequent minimization of lattice energy. This procedure was found to have no influence on the final result: using lattice energy minimization from the outset gives the same structure, but at greater computational expense. The lattice energy and crystallographic data are those extracted from the GULP minimizations, whereas coordination sequences, bond distances and angles were calculated with *zeoT-sites* (Version 1.2; Sastre & Gale, 2001). The connectivity was additionally checked with the software tool *KRIBER* (Version 1.1; Bialek, 1995). Additional calculations were carried out using *Cerius<sup>2</sup>* software (Molecular Simulations Inc., 1999).

Table 1 (continued)

Structure	$\vartheta$	$\Delta E_{\text{quartz}}$ (kJ mol <sup>-1</sup> )	$F_D$ (T sites per 1000 Å <sup>3</sup> )	Coordination sequence																
2_9	73.85	127.41	13.56	4 6 8 14 20 30 45 54 73 98																
2_60	79.89	131.67	16.65	4 7 10 14 22 34 42 58 78 94																
2_80	87.12	142.73	16.21	4 8 14 26 45 68 93 125 171 223																
2_42	104.27	164.99	17.94	4 11 22 35 52 76 109 148 189 232																
2_4	107.62	186.37	6.48	4 9 17 29 48 70 100 138 175 222																
2_36	166.29	262.64	12.30	4 11 20 36 58 81 112 146 189 240																
2_69	189.35	292.92	14.38	4 10 18 28 42 59 80 105 134 168																
				4 5 8 16 18 24 36 48 63 72																
				4 8 10 15 22 26 38 54 64 80																
				4 8 13 20 29 41 56 72 89 110																
				4 9 16 24 33 44 58 76 97 120																
				4 8 17 29 46 68 91 117 154 184																
				4 9 17 28 49 69 92 119 151 184																

Structural figures were prepared using *GDIS* (SourceForge, 2004) and *POV-Ray* (Persistence of Vision Raytracer Pty. Ltd, 2004; Henson *et al.*, 1994). The lattice energy,  $\Delta E_{\text{quartz}}$ , given in Table 1, is relative to that of  $\alpha$ -quartz, calculated using the same potential model, and is thus analogous to the heat of transition reported for several high-silica zeolites (Henson *et al.*, 1994; Petrovic *et al.*, 1993; Navrotsky *et al.*, 1995; Hu *et al.*, 1995; Piccione *et al.*, 2000, 2001, 2002; Moloy *et al.*, 2002).

### 2.1. The feasibility factor

The well established relationship between framework density and calculated lattice energy (Foster *et al.*, 2001, 2003; Foster, Friedrichs *et al.*, 2004; Foster, Simperler *et al.*, 2004; Simperler *et al.*, 2004) was confirmed experimentally (Henson *et al.*, 1994) for known zeolites. Using the standard least-squares technique, a straight line was fitted to 145 data points obtained from minimizing quartz and all the known zeolite topologies in a purely siliceous form (Fig. 1). We excluded the four non-silicate structure types which substantially deviate from the rest: WEI (calcium beryllphosphate), CZP (sodium zincophosphate), OSO (potassium beryllsilicate) and RWY (gallium germanium sulfide). The line of best fit has the formula  $y = -1.4433x + 40.3904$ , where  $x$  is the framework density ( $F_D$ ) and  $y$  is  $\Delta E_{\text{quartz}}$ . The feasibility factor,  $\vartheta$ , is then simply the dimensionless deviation of a data point ( $x_1, y_1$ ) from the line of best fit, given by the vertical offset  $\vartheta = |1.4433x_1 + y_1 + 40.3904|/1.4433$ . Being formally independent of the framework density, the feasibility factor  $\vartheta$  is thus a convenient way of discriminating between candidate structures and can be compared with the values obtained from known zeolite structures. We minimized all the known zeolite topologies as silica polymorphs, regardless of the actual composition in which they occur. We believe that  $\vartheta$  is a better gauge of the feasibility of the structure than  $\Delta E_{\text{quartz}}$  alone, as evidenced by the fact that seven of the ten lowest  $\vartheta$  values in Table 1 belong to structures with known zeolite topologies. A ranking in order of ascending  $\Delta E_{\text{quartz}}$  would, in contrast, produce only four values. Virtually all of the topologies which

are known in the form of silicates, aluminosilicates or aluminophosphates, including those with low levels of heteroatom substitution, have  $\vartheta < 5$ . This reflects the similarity of the preferred geometry between (alumino)silicates and AlPOs. The highest values of  $\vartheta$  are 5.03 for AFY (Co-AlPO-50), which has 19% framework cobalt, and 5.18 for AHT, only known as the thermally unstable material AlPO-H2. By analogy, we define structures with  $\vartheta < 5$  as feasible ‘conventional’ zeolites, *i.e.* those for which natural zeolites along with high-silica and AlPO forms are known. Framework types with

more ‘exotic’ compositions have  $\vartheta > 5$ . For example, the zincosilicates VNI, VSV and RSN have  $\vartheta$  of 5.75, 6.07 and 6.09, respectively. Beryllsilicates, generally containing three rings, also have higher  $\vartheta$ , *e.g.* LOV (6.51), NAB (10.99) and OSO (23.30), while the beryllphosphate weinebeneite has  $\vartheta = 12.24$  and the zincophosphate CZP  $\vartheta = 20.92$ . We therefore propose that  $\vartheta$  values up to 25 indicate that the topology may be feasible in the form of an ‘oxide’ material. Above this, we note that for RWY, the only zeotype structure known solely as a framework sulfide,  $\vartheta = 51.69$ . Many other compositions, such as metal-organic frameworks, are of course possible. This means that although a structure may be deemed highly unfeasible as a zeolite, it may exist in other chemical forms. Also, the precise value of  $\vartheta$  will be an unreliable guide in the high region, since it is based only on a silica model. In order to gauge the feasibility of a particular topology in a different composition, it would be necessary to carry out separate series of computations, taking into account the actual composition.

The *Cerius<sup>2</sup>* software suite (Molecular Simulations Inc., 1999) was used for visualizing and manipulating the structures and for calculating free volumes, space-group symmetry and other parameters. In addition to calculating the energetics of the hypothetical structures, it is important to compare the calculated values with the values for all known zeolite frameworks. Thus, all relevant properties were also calculated for the purely siliceous forms of all known zeolite topologies. Lattice energies were calculated relative to  $\alpha$ -quartz, the most stable form of the mineral at ambient temperature.

The ‘available volume’, defined as the difference between the volume of the unit cell and the effective volume of all the atoms, depends on the van der Waals radius used for each atom. ‘Occupiable volume’ is the volume which can be occupied by a probe molecule with a given radius as it probes the surface of the structure. The ‘accessible volume’ is determined by tracing out the volume by the centre of the probe molecule as it follows the structure contours, but with the extra requirement that the probe must enter the unit cell from the outside *via* sufficiently wide pores or channels. The accessible volume gives an indication of the space available within each

structure for applications in molecular sieving and catalysis. The calculations of the accessible volume were performed using the Free Volume module of the *Cerius*<sup>2</sup> package, which applies the Connolly (1985) method consisting of 'rolling' a probe molecule with a given radius over the van der Waals

surface of the framework atoms. We have used a probe molecule with a radius of 1.4 Å (such as water) and 1.32 and 0.9 Å for the radii of O and Si atoms, respectively. The void volume, enclosed within the Connolly surface, was calculated first. The accessible volume was then calculated by requiring the probe molecule to enter the unit cell from the outside.

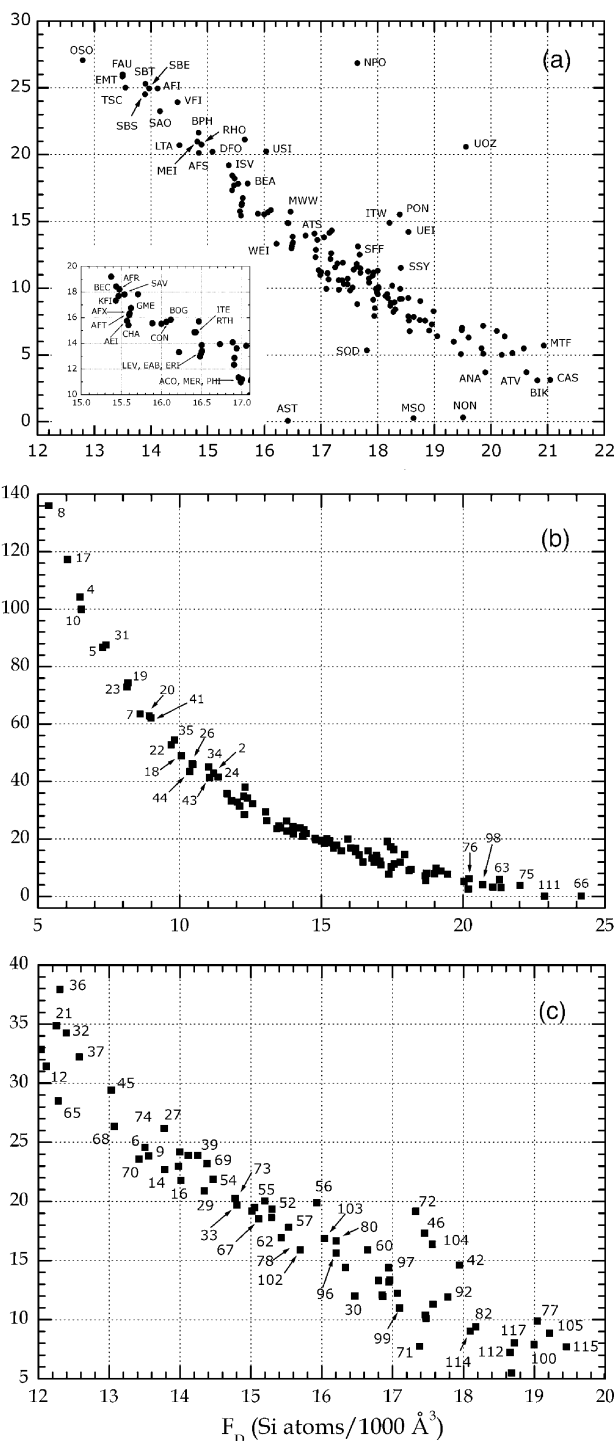
### 3. Results and discussion

Of the 117 structures, eight could not be optimized, either because refinement was not possible or because of failure during minimization, usually resulting in loss of the original network topology. The remaining 109 structures are described below. For the most part, these minimized smoothly without any loss of symmetry, although there are a few whose low-energy symmetry is lower than that of the original space group. In these instances, the original space group is shown in parentheses in Table 2.

Figs. 1(a) and (b) show plots of framework energy relative to  $\alpha$ -quartz,  $E_F$ , versus the framework density,  $F_D$ , for all known zeolites. Relative framework energies of the hypothetical binodal frameworks range from 11.15 kJ mol<sup>-1</sup> (structure 2\_114) to as much as 515.43 kJ mol<sup>-1</sup> (structure 2\_72) (Fig. 1c). Fig. 1(d) plots the framework energy versus the framework density for the hypothetical binodal structures with energies below 30 kJ mol<sup>-1</sup>, the range considered as the most 'desirable', and with framework densities typical of the known zeolites.

Fig. 2(a) shows a plot of accessible volume versus framework density for the known structural types and Figs. 2(b) and (c) the corresponding plot for hypothetical binodal zeolites. Low framework density structures are of particular interest as they have very high accessible free volumes. Of the structures with framework densities below 18 Si atoms/1000 Å<sup>3</sup>, structures 2\_57, 2\_58, 2\_59, 2\_82, 2\_85, 2\_86, 2\_87, 2\_91, 2\_95, 2\_96, 2\_102, 2\_103, 2\_106, 2\_108, 2\_109, 2\_110, 2\_112, 2\_113, 2\_114 and 2\_117 are energetically stable (Fig. 1c). Many hypothetical structures have dense frameworks, which are largely inaccessible. However, as many known zeolite topologies have low accessible volumes (Fig. 2a), a structure cannot be ruled out as a feasible topology on the basis of a low accessible free volume, even though it may be of no interest to scientists studying sorption, ion exchange or catalysis. A plot of framework density for known zeolites and for dense silicate frameworks against the size of the smallest ring in the structure (Brunner & Meier, 1989) shows that very open frameworks with low  $F_D$  have the largest number of four- and three-membered rings and that there is a gap in  $F_D$  between compact minerals, such as quartz and tridymite, and the zeolite frameworks. The lower boundary of  $F_D$  for known zeolites is from about 11 tetrahedral atoms per 1000 Å<sup>3</sup> in materials with four-membered rings to about 17 tetrahedral atoms in materials with 5+ rings, where the plus sign signifies that some tetrahedral atoms are associated only with the larger rings.

Fig. 3 plots the framework energy with respect to  $\alpha$ -quartz for the known zeolitic structures and the hypothetical binodal structures versus the accessible volume, thus combining



**Figure 2**  
Accessible volume (Å<sup>3</sup> per Si atom) versus framework density for (a) all known zeolitic structure types; (b) hypothetical binodal zeolitic structures; (c) structures with accessible volumes below 40 Å<sup>3</sup> per Si atom.

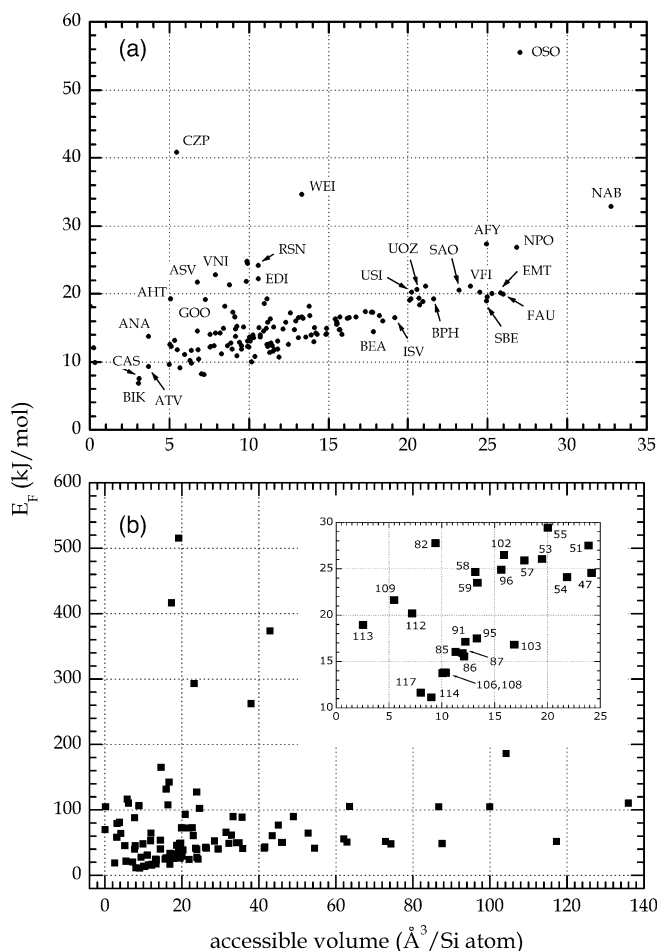
information contained in Figs. 1 and 2. Structures of the greatest practical interest are those with low energies and large volumes (see inset in Fig. 3*b*). Full details of all the structures have recently been published elsewhere (Foster, Simperler *et al.*, 2004). Crystallographic CIF files from which powder X-ray diffraction patterns can be easily calculated are given as supplementary information.<sup>1</sup>

The structures have been divided into 15 families, the members of which share a common building scheme or structural unit. As explained above, the building units used do not necessarily equate to SBUs or PerBUs in the strict sense. We also note that the allocation of a structure to a certain family is not unequivocal: there are several structures which could equally well be assigned to more than one family. The order in which the various families are discussed is dictated by the feasibility factor of the most feasible structure in that family. Selected members of a particular family are shown in Figs. 4–9 in the same order, whereas a full description of all members is available in the electronic supplement. The more feasible structures will thus be encountered earlier in the following sections, with the exception of the ‘orphan family’ which contains several chemically feasible members. In describing the various structures, we use standard nomenclature from the zeolite literature. For instance, ‘D6R’ refers to a double six-ring unit. In describing polyhedral cages or units, the  $[M^xN^y]$  system adopted by Smith (1988) is also used, where  $(M, N)$  is the number of edges defining a given face and  $(x, y)$  is the number of times that face appears in the polyhedron. Results are also tabulated in Table 1 (in order of  $\vartheta$ ) and Table 2 (in numerical order of the structures). Table 1 gives  $\vartheta$ ,  $\Delta E_{\text{quartz}}$ , the framework density and the coordination sequences of the  $T$  sites. Table 2 gives the crystallographic data.

### 3.1. ABC-6 family

Of the 109 refinable binodal structures, 13 can be described using the building scheme for the ABC-6 family (van Koningsveld, 2004). Six of these are known frameworks: 2<sub>89</sub> = ERI, 2<sub>84</sub> = EAB, 2<sub>90</sub> = SAT, 2<sub>83</sub> = LEV, 2<sub>107</sub> = LOS and 2<sub>78</sub> = AFX. The PerBU of the family consists of a hexagonal array of isolated six-membered rings, which are related by pure translations along [100] and [010]. A three letter code ( $A, B$  and  $C$ ) gives the connection mode of the layers along [001]. The six-membered rings of  $A$  are centred at  $(0,0)$ , while layer  $B$  is shifted by  $(+2/3a, +1/3b)$  and layer  $C$  by  $(+1/3a, +2/3b)$ . The connection between six-rings in adjacent layers is invariably *via* four-rings. In the (001) projection, there is a close similarity between all the structures of this family, epitomized by that of 2<sub>106</sub> (Fig. 4*a*), where the hexagonal array of six-rings, interspersed by four-rings, is clearly evident. Each structure is uniquely characterized by its [001] stacking sequence and the stacking sequences of the 13 structures (in order of their ‘thermodynamic feasibility’) are

ABBACBBC( $A$ ) for 2<sub>87</sub>, ACAABA( $A$ ) for 2<sub>89</sub> (ERI), ACCABB( $A$ ) for 2<sub>84</sub> (EAB), AABABBCBCCAC( $A$ ) for 2<sub>90</sub> (SAT), ABBC( $A$ ) for 2<sub>86</sub>, AACBBACCB( $A$ ) for 2<sub>83</sub> (LEV), ABAC( $A$ ) for 2<sub>107</sub> (LOS), ACABABCBC( $A$ ) for 2<sub>110</sub>, ACABCBA( $A$ ) for 2<sub>106</sub>, ACACBABACBCB( $A$ ) for 2<sub>108</sub>, ACCAABBA( $A$ ) for 2<sub>78</sub> (AFX), ACCCBBA( $A$ ) for 2<sub>40</sub>, and AAAACCCCB( $A$ ) for 2<sub>33</sub>. 2<sub>87</sub>, 2<sub>89</sub>, 2<sub>84</sub>, 2<sub>107</sub>, 2<sub>106</sub> and 2<sub>78</sub>, which have hexagonal symmetry, space group  $P6_3/mmc$ , while 2<sub>90</sub>, 2<sub>83</sub>, 2<sub>110</sub>, 2<sub>108</sub>, 2<sub>40</sub> and 2<sub>33</sub> (all  $R\bar{3}m$ ) and 2<sub>86</sub> ( $P\bar{3}m1$ ) are trigonal. The ABC-6 structures, both known and hypothetical, are among the most thermodynamically favoured as silica polymorphs and, as can be seen from Table 1, have high chemical feasibilities ( $0.08 < \vartheta < 0.98$ ), except for 2<sub>40</sub> and 2<sub>33</sub> which have  $\vartheta$  of 14.97 and 20.83, respectively. The ABC-6 structures may also be thought of in terms of stacks, or chains, of cages linked parallel to the [001] direction through six-rings and, depending on symmetry, there are either one or two distinct types of stack. For example, the most feasible structure 2<sub>87</sub> (Figs. 4*b* and *c*) contains both the  $[4^96^28^3]$  gmelinite cages and  $[4^96^88^3]$  EAB cages, which alternate along (001) (Fig. 4*c*). Parallel to these are stacks of alternating sodalite cages and double six-rings



**Figure 3** Framework energy with respect to  $\alpha$ -quartz versus accessible volume ( $\text{\AA}^3$  per Si atom) for (a) all known zeolitic structure types; (b) hypothetical binodal zeolitic structures. Hypothetical structures of particular chemical interest are identified in the inset.

<sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK5018). Services for accessing these data are described at the back of the journal.



Table 2

Space groups and unit-cell dimensions of 109 hypothetical binodal zeolites, optimized as purely siliceous structures.

Structure	Space-group symbol	Space-group number	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)
2_4	$Im\bar{3}m$	229	24.5550	24.5550	24.5550	90	90	90
2_5	$Im\bar{3}m$	229	23.6252	23.6252	23.6252	90	90	90
2_6	$Pn\bar{3}m$	224	19.2265	19.2265	19.2265	90	90	90
2_7	$P\bar{4}3m$	215	14.0784	14.0785	14.0785	90	90	90
2_8	$Im\bar{3}m$	229	29.9045	29.9046	29.9046	90	90	90
2_9	$R\bar{3}m$	166	20.6871	20.6871	10.7470	90	90	120
2_10	$Im\bar{3}m$	229	30.8610	30.8610	30.8610	90	90	90
2_12	$I4_1/amd$	141	15.1769	15.1769	17.2033	90	90	90
2_13	$Fm\bar{3}m$	225	17.4521	17.4521	17.4521	90	90	90
2_14	$I4/mmm$	139	11.5929	11.5929	12.9540	90	90	90
2_15	$Pm\bar{3}n$	223	13.6367	13.6367	13.6367	90	90	90
2_16	$P4_2/mnm$	136	10.2171	10.2171	16.3964	90	90	90
2_17	$Im\bar{3}m$	229	31.6666	31.6666	31.6666	90	90	90
2_18	$Im\bar{3}m$	229	18.1332	18.1332	18.1332	90	90	90
2_19	$Im\bar{3}m$	229	26.0211	26.0211	26.0211	90	90	90
2_20	$Pm\bar{3}m$	221	17.5191	17.5191	17.5191	90	90	90
2_21	$Fm\bar{3}m$	225	31.5256	31.5256	31.5256	90	90	90
2_22	$Pm\bar{3}m$	221	19.5087	19.5087	19.5087	90	90	90
2_23	$Fm\bar{3}m$	225	32.8255	32.8255	32.8255	90	90	90
2_24	$Pm\bar{3}m$	221	14.6896	14.6896	14.6896	90	90	90
2_25	$Fm\bar{3}m$	225	30.1897	30.1897	30.1897	90	90	90
2_26	$Fm\bar{3}m$	225	30.2151	30.2151	30.2151	90	90	90
2_27	$Fm\bar{3}m$	225	27.5480	27.548	27.5480	90	90	90
2_28	$Im\bar{3}$	204	16.0155	16.0155	16.0155	90	90	90
2_29	$Fd\bar{3}c$	228	29.9172	29.9172	29.9172	90	90	90
2_30	$Pn\bar{3}m$	224	15.3879	15.3879	15.3879	90	90	90
2_31	$R\bar{3}m (Fd\bar{3}m)$	166 (227)	26.3028	26.3028	64.9314	90	90	120
2_32	$Im\bar{3}m$	229	24.9270	24.9270	24.9270	90	90	90
2_33	$R\bar{3}m$	166	13.1741	13.1741	32.3570	90	90	120
2_34	$Im\bar{3}m$	229	25.9183	25.9183	25.9183	90	90	90
2_35	$Fd\bar{3}m$	227	30.8413	30.8416	30.8413	90	90	90
2_36	$Pm\bar{3}m$	221	19.8342	19.8342	19.8342	90	90	90
2_37	$Pn\bar{3}m$	224	19.6887	19.6887	19.6887	90	90	90
2_39	$P1 (Im\bar{3}m)$	1 (229)	21.5940	21.6260	30.2151	90.1262	89.9558	90.0775
2_40	$R\bar{3}m$	166	13.2084	13.2084	23.8034	90	90	120
2_41	$Im\bar{3}m$	229	25.2127	25.2127	25.2127	90	90	90
2_42	$Im\bar{3}m$	229	20.0209	20.0209	20.0209	90	90	90
2_43	$Fm\bar{3}m$	225	25.9040	25.9040	25.9040	90	90	90
2_44	$P\bar{4}3m$	215	11.3123	11.3124	11.3124	90	90	90
2_45	$Pm\bar{3}m$	221	17.6786	17.6786	17.6786	90	90	90
2_46	$Pn\bar{3}m$	224	15.4919	15.4919	15.4919	90	90	90
2_47	$Pm\bar{3}m$	221	19.0003	19.0003	19.0003	90	90	90
2_48	$Pm\bar{3}n$	223	16.7613	16.7613	16.7613	90	90	90
2_50	$P\bar{3}1m$	162	12.3351	12.3351	8.6007	90	90	120
2_51	$P6_2/mcm$	193	12.3340	12.3340	17.2043	90	90	120
2_52	$Pn\bar{3}m$	224	16.7584	16.7584	16.7584	90	90	90
2_53	$Pn\bar{3}m$	224	18.5448	18.5448	18.5448	90	90	90
2_54	$I4/mmm$	139	14.8438	14.8438	20.0782	90	90	90
2_55	$P6_2/mcm$	193	13.7562	13.7562	19.2727	90	90	120
2_56	$P\bar{3}1m$	162	13.7003	13.7003	9.2686	90	90	120
2_57	$I4/mmm$	139	14.0993	14.0993	15.5435	90	90	90
2_58	$I4/mmm$	139	13.5265	13.5265	20.6385	90	90	90
2_59	$P4/nmm$	129	13.5133	13.5133	10.3319	90	90	90
2_60	$Im\bar{3}m$	229	17.9320	17.9320	17.9320	90	90	90
2_61	$I4_1/amd$	141	16.3875	16.3875	10.9441	90	90	90
2_62	$Pm\bar{3}m$	221	14.5985	14.5985	14.5985	90	90	90
2_63	$I\bar{4}m2$	119	12.6142	12.6142	9.4486	90	90	90
2_64	$Pm\bar{3}m$	221	18.3419	18.3419	18.3419	90	90	90
2_65	$Ia\bar{3}$	206	18.0311	18.0311	18.0311	90	90	90
2_67	$Ia\bar{3}d$	230	19.9520	19.9520	19.9520	90	90	90
2_68	$I4_1/amd$	141	15.1043	15.1043	10.7274	90	90	90
2_69	$R\bar{3}m$	166	16.6853	16.6853	20.9554	90	90	120
2_70	$Pm\bar{3}m$	221	13.8940	13.8940	13.8940	90	90	90
2_71	$P2_13$	198	14.0298	14.0298	14.0298	90	90	90
2_73	$Fd\bar{3}m$	227	29.6184	29.6184	29.6184	90	90	90
2_74	$Fm\bar{3}m$	225	30.4872	30.4872	30.4872	90	90	90
2_75	$Fd\bar{3}m$	227	25.9368	25.9368	25.9368	90	90	90
2_76	$P\bar{4}3m$	215	13.3418	13.3418	13.3418	90	90	90
2_77	$Pn\bar{3}m$	224	15.5787	15.5787	15.5787	90	90	90

(D6R). The structure 2\_40, which is less dense, is quite interesting as it has large cages linked through elongated 10- and 12-rings, respectively (Fig. 4d and e).

### 3.2. [3<sup>2</sup>5<sup>6</sup>] family

Four structures (2\_103, 2\_55, 2\_56 and 2\_104) are built up from columns of [3<sup>2</sup>5<sup>6</sup>] polyhedral units (Fig. 4g) arranged hexagonally so as to give 12-membered ring channels along the *c* direction (Fig. 4f). The [3<sup>2</sup>5<sup>6</sup>] units are linked by sharing their ‘terminal’ three-membered ring windows (Fig. 4h) in structures 2\_103 and 2\_104, while in structures 2\_55 and 2\_56 these small cage units are separated by a [3<sup>2</sup>4<sup>3</sup>] unit (*i.e.* a trigonal prism or D3R; Fig. 4i). None of these four are known structures, although 2\_103 is expected to be highly chemically feasible ( $\vartheta = 0.30$ ). Three further members of this family, 2\_112, 2\_102 and 2\_80, also contain the [3<sup>2</sup>5<sup>6</sup>] unit (Fig. 4g), but with different building patterns. For example, in 2\_112 the [3<sup>2</sup>5<sup>6</sup>] units are linked *via* single oxygen bridges, while in 2\_102 and 2\_80 the units are linked *via* double oxygen bridges (Fig. 4j). Both 2\_112 and 2\_102 are highly feasible, with  $\vartheta = 4.66$  and 6.08, respectively, as opposed to 2\_80 which has  $\vartheta = 87.12$ .

### 3.3. AWW family

The nine structures which we describe as members of the ‘AWW family’ share a small [4<sup>6</sup>6<sup>4</sup>] cage as the common building unit (Fig. 5a). Six of these structures, 2\_88 (which has the actual AWW topology), 2\_85, 2\_59, 2\_58, 2\_100 and 2\_63, are tetragonal, with columns of larger cages parallel to [001] and having eight-ring windows as the maximum pore diameter in that direction. The archetypal example is the AWW [4<sup>8</sup>6<sup>8</sup>8<sup>2</sup>] cage (Fig. 5b), which stacks through shared eight-rings. Fig. 5(c) shows the [001] projection of 2\_85, which is typical of this series.

Depending on the linkage pattern of the [4<sup>6</sup>6<sup>4</sup>] building units along [001], different types of large cage are defined. AWW, 2\_59, 2\_100 and 2\_63

Table 2 (continued)

Structure	Space-group symbol	Space-group number	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)
2_78	<i>P6<sub>3</sub>/mmc</i>	194	13.5479	13.5479	19.3503	90	90	120
2_79	<i>Im<math>\bar{3}m</math></i>	229	21.2424	21.2424	21.2424	90	90	90
2_80	<i>Im<math>\bar{3}m</math></i>	229	18.0938	18.0938	18.0938	90	90	90
2_81	<i>I4/mmm</i>	139	13.9993	13.9993	10.2051	90	90	90
2_82	<i>Pn<math>\bar{3}m</math></i>	224	15.8240	15.8240	15.8240	90	90	90
2_83	<i>R<math>\bar{3}m</math></i>	166	12.9786	12.9786	22.4610	90	90	120
2_84	<i>P6<sub>3</sub>/mmc</i>	194	12.9887	12.9887	14.9436	90	90	120
2_85	<i>I4/mmm</i>	139	13.2812	13.2812	15.4875	90	90	90
2_86	<i>P<math>\bar{3}m1</math></i>	164	12.7931	12.7931	10.0490	90	90	120
2_87	<i>P6<sub>3</sub>/mmc</i>	194	12.7982	12.7982	20.0706	90	90	120
2_88	<i>P4/nmm</i>	129	13.5200	13.5199	7.6115	90	90	90
2_89	<i>P6<sub>3</sub>/mmc</i>	194	12.9122	12.9122	15.1051	90	90	120
2_90	<i>R<math>\bar{3}m</math></i>	166	12.7260	12.7259	30.3678	90	90	120
2_91	<i>I4/mcm</i>	140	13.9768	13.9768	19.1953	90	90	90
2_92	<i>P4/nbm</i>	125	13.9490	13.9490	9.2497	90	90	90
2_93	<i>Im<math>\bar{3}m</math></i>	229	17.2697	17.2697	17.2697	90	90	90
2_94	<i>C2 (Fd<math>\bar{3}m</math>)</i>	5 (227)	29.4382	29.3841	20.7989	90	90	90
2_95	<i>I4/mmm</i>	139	12.2058	12.2058	19.1794	90	90	90
2_96	<i>Im<math>\bar{3}</math></i>	204	16.4413	16.4413	16.4413	90	90	90
2_97	<i>Pm<math>\bar{3}n</math></i>	223	16.1973	16.1973	16.1973	90	90	90
2_98	<i>P4<sub>3</sub>2</i>	213	11.5642	11.5642	11.5642	90	90	90
2_99	<i>Pm<math>\bar{3}</math></i>	200	12.8171	12.8171	12.8171	90	90	90
2_100	<i>I<math>\bar{4}m2</math></i>	119	12.8690	12.8691	7.6292	90	90	90
2_101	<i>Fm<math>\bar{3}m</math></i>	225	13.4592	13.4592	13.4592	90	90	90
2_102	<i>R<math>\bar{3}m</math></i>	166	12.6141	12.6141	16.6417	90	90	120
2_103	<i>P6<sub>3</sub>/mcm</i>	193	13.6152	13.6152	13.9813	90	90	120
2_104	<i>P<math>\bar{3}1m</math></i>	162	13.4810	13.4810	6.5129	90	90	120
2_105	<i>P1 (R<math>\bar{3}c</math>)</i>	1 (167)	10.6747	16.8789	16.9018	67.8079	86.0781	86.1532
2_106	<i>P6<sub>3</sub>/mmc</i>	194	12.4093	12.4093	15.4571	90	90	120
2_107	<i>P6<sub>3</sub>/mmc</i>	194	12.3972	12.3972	10.3205	90	90	120
2_108	<i>R<math>\bar{3}m</math></i>	166	12.4186	12.4186	30.8573	90	90	120
2_109	<i>Pn<math>\bar{3}m</math></i>	224	17.2562	17.2562	17.2562	90	90	90
2_110	<i>R<math>\bar{3}m</math></i>	166	12.4060	12.4060	23.1948	90	90	120
2_111	<i>P4<sub>3</sub>2</i>	213	11.6324	11.6324	11.6324	90	90	90
2_112	<i>P2<sub>1</sub>3</i>	198	13.7019	13.7019	13.7019	90	90	90
2_113	<i>Fddd</i>	70	7.4170	13.5469	23.6645	90	90	90
2_114	<i>I4/mcm</i>	140	13.7055	13.7055	14.1225	90	90	90
2_115	<i>P4/nbm</i>	125	13.4128	13.4128	6.8567	90	90	90
2_116	<i>I432</i>	211	16.4510	16.4519	16.4510	90	90	90
2_117	<i>P4<sub>2</sub>/mm</i>	136	7.1839	7.1839	12.4079	90	90	90

have only one type of eight-ring channel cage each, whilst in 2\_85 two alternating types of larger cage are thus defined, [4<sup>8</sup>6<sup>12</sup>8<sup>2</sup>] and [4<sup>8</sup>6<sup>4</sup>8<sup>2</sup>] (also found in the structures SAS and ATN respectively). Structures AWW, 2\_58, 2\_59 and 2\_85 fall within the feasible range, with  $\vartheta = 0.32$ – $6.04$ , while 2\_100 ( $\vartheta = 22.42$ ) and 2\_63 ( $\vartheta = 73.83$ ) are less feasible.

There are also three cubic structures, which contain the same building unit (2\_109, 2\_97 and 2\_60), with 2\_109 being by far the most feasible of the three ( $\vartheta = 5.67$ ). For these three structures, the [4<sup>6</sup>6<sup>4</sup>] units alternate with sodalite or beta cages in a chain along [100]. Structure 2\_97 ( $\vartheta = 16.99$ ) falls within the extended range of oxide feasibility, whereas 2\_60 ( $\vartheta = 80.04$ ) does not.

### 3.4. Supercage family

There are 11 structures which contain sodalite or LTA (alpha) cages linked by smaller prismatic units in such a way that it also generates much larger cages. All the structures have cubic or pseudo-cubic symmetry, as can be seen in the

[100] view of 2\_45 (Fig. 5e). Structure 2\_74 has the framework of the mineral tschörtnerite (TSC) with both sodalite and alpha cages linked *via* D6R (Fig. 5f), thus defining the large TSC cage (Fig. 5g). The remaining structures will be discussed with respect to structural similarities and not by their chemical feasibility factor,  $\vartheta$ .

Structures 2\_35 (Fig. 5h) and 2\_31 are composed of sodalite cages linked tetrahedrally *via* D6R and thus form a series together with the FAU structure. 2\_35 and 2\_31 are both feasible as oxide materials, with  $\vartheta$  of 10.69 and 13.16, respectively. 2\_45 (Fig. 5i) and 2\_36 can similarly be imagined as belonging to a series with RHO, a structure formed by alpha cages linked octahedrally *via* D8R. Both have *Pm $\bar{3}m$*  symmetry and 2\_45 is relatively feasible ( $\vartheta = 12.91$ ). 2\_24 (Fig. 5j) and 2\_20 are related to the LTA structure, since they can be generated by linking sodalite cages and D4R. They also have the same supercages as 2\_45 and 2\_36 and similar  $\vartheta$  of 13.28 and 16.11, respectively. Structures 2\_27 (Fig. 7k) and 2\_21 can also be considered part of a series with LTA, except in this case it is the alpha cages which are retained and the linkages between them expanded. The final pair, 2\_39 (Fig. 5l) and 2\_32, form a series derived from KFI, containing alpha cages

which are connected *via* shared D6R and are replaced by stacks of two and three D6R.

### 3.5. SAS family

These structures are analogous to the AWW family as they contain stacks of large cages linked unidirectionally by eight-rings. Fig. 6(a) shows the [001] projection of structure 2\_54, typical of all four tetragonal structures belonging to this family and having *I4/mmm* space-group symmetry [2\_54, 2\_57, 2\_81 (SAS) and 2\_95]. The basic building units may be thought of as smaller polyhedra arranged in parallel chains: in the case of 2\_81 the basic units are D6R hexagonal prisms, which form a chain by sharing four-rings, 2\_95 is a highly feasible ( $\vartheta = 0.93$ ) structure in which [4<sup>4</sup>5<sup>4</sup>] units are linked into chains *via* four-rings (Fig. 6b); in 2\_57 an additional D4R is interposed between the alternating D6R and 2\_54 is built analogously from chains of alternating D8R and D4R. Aside from SAS and 2\_95, both 2\_54 and 2\_57 are also quite feasible as zeolites ( $\vartheta = 3.18$  and 5.51, respectively).

### 3.6. $[4^25^8]$ family

These structures have a small  $[4^25^8]$  cage as the building unit (Fig. 6*d*). In four of the structures, these units are linked into chains through the four-rings which cap the cages. The structures are tetragonal with  $[4^25^8]$  chains running along  $[001]$  and have large cages accessible through eight-rings. The projection of 2\_91 along  $[001]$  is typical of this family (Fig. 6*c*). Structure 2\_91 is the most feasible of these structures ( $\vartheta = 0.95$ ) and has  $[4^25^8]$  cages linked through D4R, with a chain repeat motif of two cages and two D4R. In 2\_114, another highly feasible structure with  $\vartheta = 2.17$ , the cages are directly linked through a shared four-ring. Structures 2\_92 and 2\_115 are analogous to structures 2\_91 and 2\_114, respectively, but with only half the

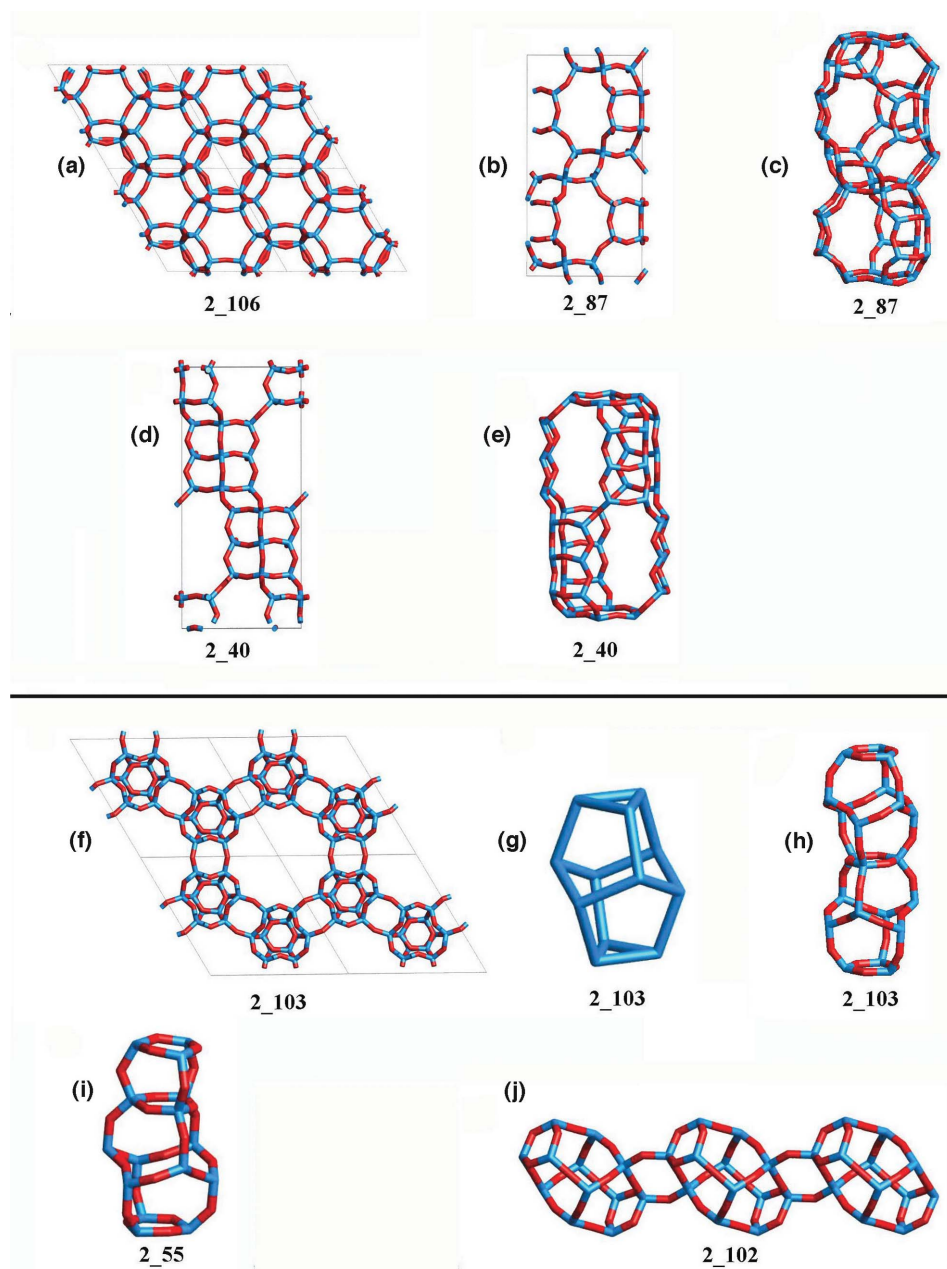
chain repeat distance. Both structures are far less feasible, as is a fifth structure, 2\_116 (Figs. 6*e* and *f*), in which the  $[4^25^8]$  units are linked into chains *via* pairs of  $T-O-T$  linkages (Fig. 6*f*). In the latter, the chains are interconnected so as to run in all three directions of the cubic lattice and the structure also contains sodalite cages, each of which shares its four-ring windows with  $[4^25^8]$  units.

### 3.7. AST family

Structure 2\_101 (Fig. 6*g-i*) is topologically identical to the known zeolite AST (AIPO-16).<sup>33,34</sup> The structure contains the characteristic  $[4^66^{10}]$  cages (Fig. 6*i*), but may also be thought of in terms of D4R units connected through  $O-T-O$  bridges (Fig. 6*h*). In 2\_73 the D4R connect through single oxygen bridges and, apart from containing sodalite cages, the structure also possesses large tetrahedral cages with 12-ring apertures. Structure 2\_61 is tetragonal containing cages with oval-shaped ten-rings as their largest apertures. Topologically, 2\_13 (Figs. 6*j* and *l*) is a variation of the AST structure in which those  $T$  atoms which *do not* form part of D4R are replaced by the  $[3^4]$  tetrahedra of  $T$  sites, a structural feature not found in aluminosilicate zeolites, although present, for instance, in the zeotypic sulfide RWY.

### 3.8. D8R family

This family is formed by four structures which contain the double eight-ring (D8R) as a structural unit. Structure 2\_47 has a cubic structure in which the building unit may be thought of as a D8R with four D4R attached to alternate four-ring faces (Fig. 7*a*). The units do not link directly to one another, but are arranged so as to define the large  $[4^{24}6^88^{18}]$  (TSC) cages (Fig. 7*b*). Structures 2\_19 and 2\_17 form part of a homologous series of structures, together with the uninodal structure 1\_11 (Foster *et al.*, 2003), one of the nine simple uninodal tilings. The latter structure has a body-centered cubic framework based on chains of D8R and D4R, and 2\_19 has the same structure, except that the D4R in 1\_11 are replaced in 2\_19 by pairs of face-sharing D4R (Fig. 7*c*) and



**Figure 4**  
Molecular graphic illustrations of some structures from the ABC-6 and  $[3^25^6]$  families.

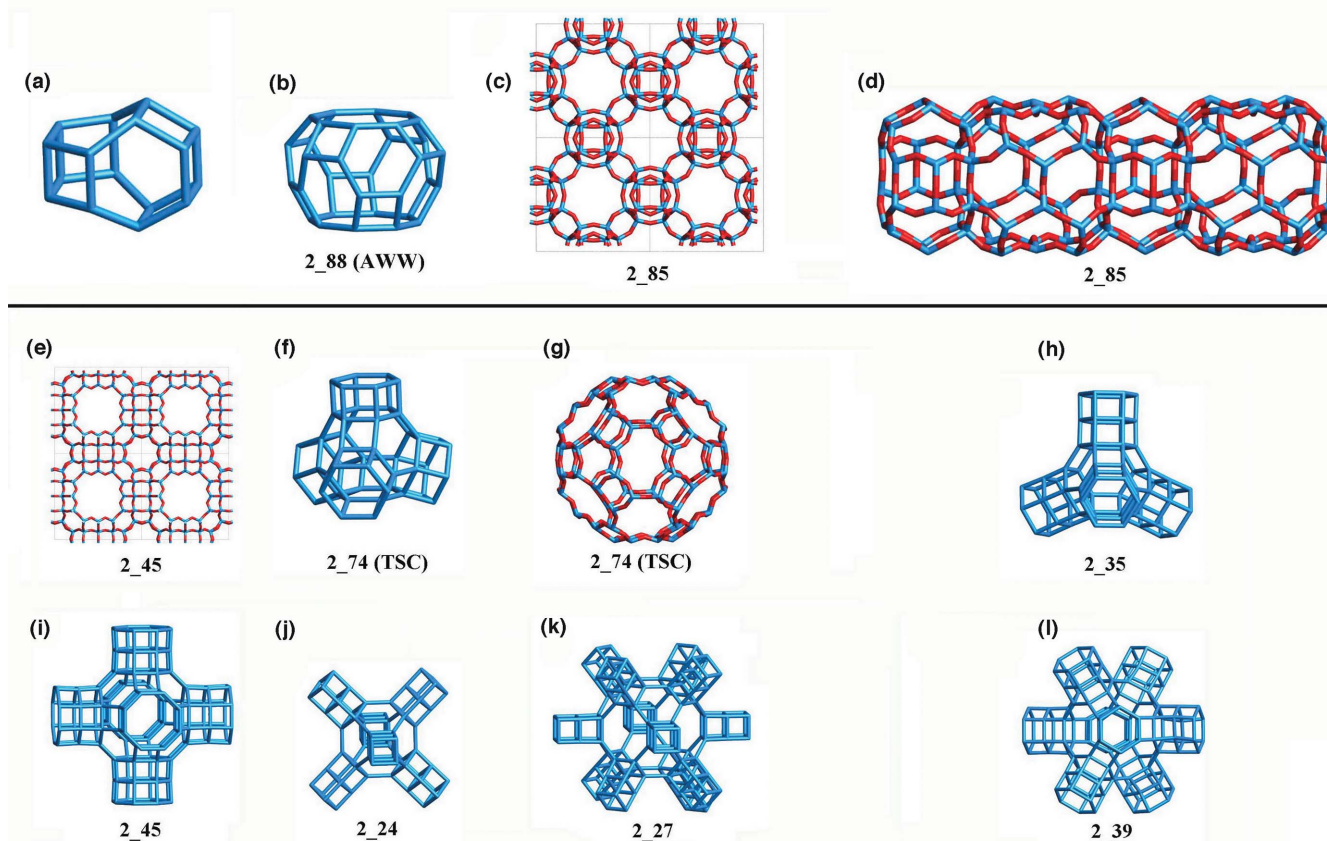
in 2<sub>17</sub> by groups of three D4R. The more complex 2<sub>34</sub> structure also contains the D8R/D4R units, but with the addition of [4<sup>6</sup>6<sup>4</sup>] AWW cages forming large cages with 12-rings as the maximum aperture (Fig. 7*d*). Topologically, the tile which corresponds to this cage is the largest among this set of binodal frameworks, with 74 faces, 144 vertices and 216 edges. Structure 2<sub>34</sub> shares the space group *Im* $\bar{3}$ *m* with both 2<sub>19</sub> and 2<sub>17</sub>. Structure 2<sub>47</sub> is thermodynamically feasible ( $\vartheta = 3.02$ ), while 2<sub>17</sub> and 2<sub>19</sub> have  $\vartheta = 13.96$  and 13.39, respectively, despite having extremely low framework densities of 8.17 and 6.05 *T* per 1000 Å<sup>3</sup>, respectively.

### 3.9. AFY family

Structure 2<sub>50</sub> is topologically identical to the known structural type AFY (AIPO-50). The secondary building unit of this family is a D4R, which in AFY form hexagonal layers (Fig. 7*e*) and are tilted with respect to the (001) plane. These layers then repeat through simple translation along *c*, most clearly seen in the (120) projection (Fig. 7*f*; van Koningsveld, 2004; Baelocher & McCusker, 2004). If, instead, the layers alternate in orientation by means of a mirror plane (*i.e.* *ABA* rather than *AA*), the hypothetical framework 2<sub>51</sub> is formed. Both have low  $\vartheta$  values: 5.03 and 5.18 for 2<sub>50</sub> and 2<sub>51</sub>, respectively, making 2<sub>51</sub> virtually as feasible as AFY.

### 3.10. D6R family

This family comprises seven structures (2<sub>6</sub>, 2<sub>30</sub>, 2<sub>53</sub>, 2<sub>75</sub>, 2<sub>76</sub>, 2<sub>77</sub> and 2<sub>82</sub>) which have in common D6R hexagonal prisms as building units. These structures are all cubic, space group *Pn* $\bar{3}$ *m*, with the exception of 2<sub>76</sub> and 2<sub>75</sub>, for which D6R (*i.e.* 6–6) may be strictly defined as a secondary building unit. The first five members of the group may be thought of in terms of chains running along [110] in which the D6R are linked by various combinations of rings. In the most feasible member of the family, 2<sub>53</sub> ( $\vartheta = 5.11$ ), the link unit includes D4R, giving rise to the characteristic motif shown in Fig. 7(*g*), where four D6R are connected to a single D4R. This structure also contains FAU supercages linked *via* the [4<sup>18</sup>8<sup>6</sup>12<sup>2</sup>] cages (Fig. 7*h*). Structure 2<sub>82</sub> is quite similar to 2<sub>53</sub>, whereas in 2<sub>77</sub> the D6R chains are linked by units of three four-rings and in 2<sub>30</sub> a spiro-5 unit links the D6R into chains. Structure 2<sub>6</sub> also contains three-rings linked into [3<sup>4</sup>] tetrahedra which connect the D6R. Finally, structures 2<sub>75</sub> and 2<sub>76</sub> are the ‘odd ones’ of the family since it is not possible to describe them using the D6R chain model. Structure 2<sub>75</sub> is very unusual as it contains both ‘regular’ and flattened sodalite cages connected through six-rings (Fig. 7*i*). Structure 2<sub>76</sub> contains (differently) distorted beta cages as well as larger cages accessible through both approximately planar six-rings



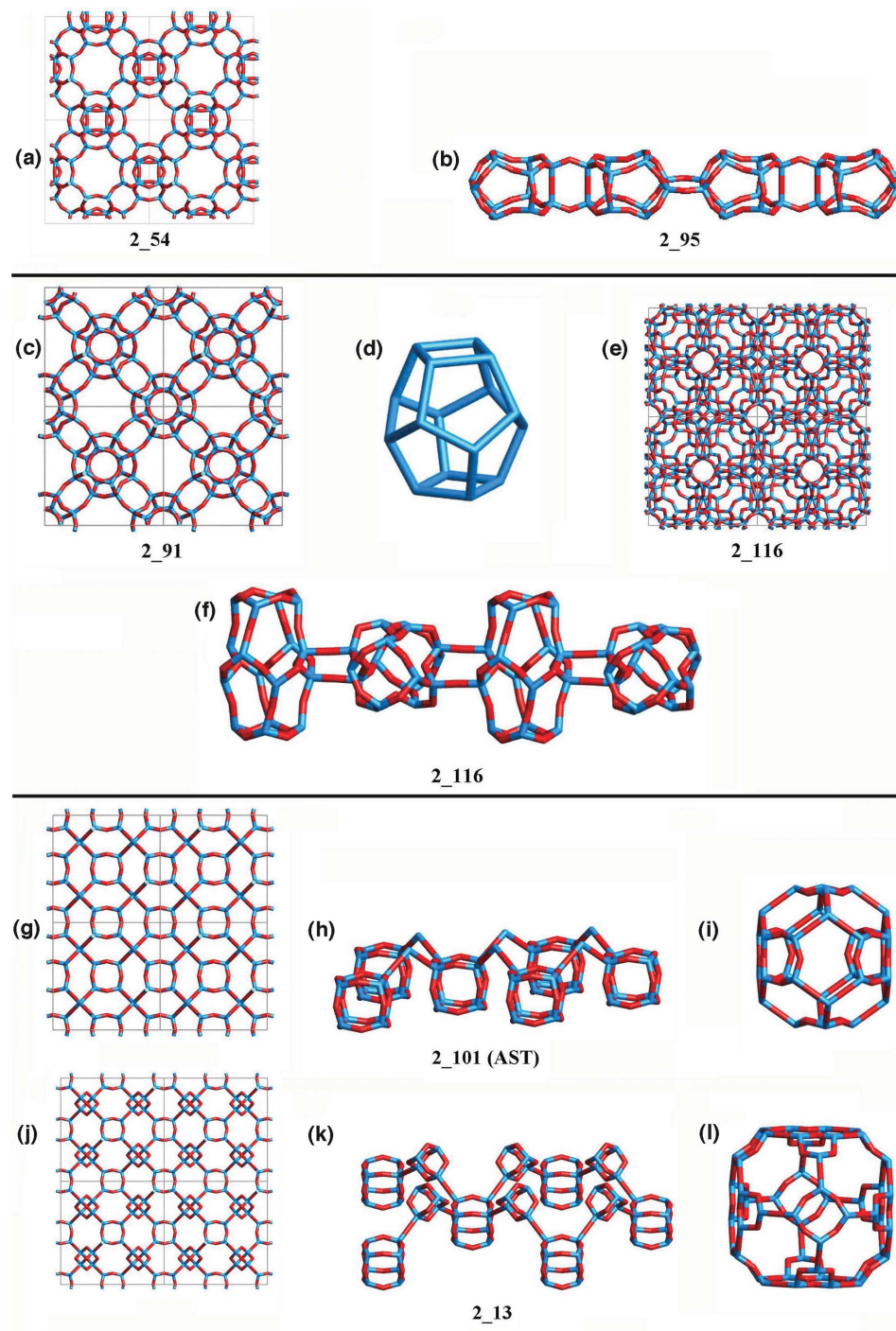
**Figure 5**  
Molecular graphic illustrations of some structures from the AWW and supercage families.

and highly curved eight-rings. Structures 2\_75, 2\_6 or 2\_76 are not expected to be chemically feasible.

### 3.11. Three- and four-ring family

These eight structures are grouped together because they contain both three- and four-membered rings, although in

other ways they are fairly different. Seven structures are cubic and five have framework densities lower than 14  $T$  per 1000  $\text{\AA}^3$ . Structure 2\_99, the most feasible structure of this family with  $\vartheta = 10.53$ , can be described as a network of corner-sharing three- and four-rings, part of which is the unit shown in Fig. 8(a). Three types of cages are found, one of which is the  $[3^88^6]$  (truncated cube, Fig. 8b). The somewhat similar 2\_62,



**Figure 6**  
Molecular graphic illustrations of structures from the SAS,  $[4^{25^8}]$  and AST families.

which has  $\vartheta = 10.97$ , also exhibits the truncated cube cage. Structure 2\_68 has a low framework density of 13.08  $T$  per 1000  $\text{\AA}^3$  and  $\vartheta = 13.82$ . Structures 2\_70 and 2\_93 have similar framework densities to that of 2\_68 (13.42 and 13.98, respectively) and  $\vartheta = 14.33$  and 28.25, making these three structures interesting candidates as zeotypes. Structure 2\_93 contains  $[3^46^4]$  cages, *i.e.* truncated tetrahedra (Fig. 8c), which link through shared three-rings to form a body-centred cubic structure. Structures 2\_18, 2\_28 and 2\_5 have much lower framework densities (10.06, 11.69 and 7.28, respectively) than conventional zeolites, and are thus much less feasible as zeotype materials.

### 3.12. $[3^24^3]$ D3R family

The common feature is a trigonal prism (a  $[3^24^3]$  unit) and we have assigned nine structures to this family. As in the previous family, many are of interest due to their low density, with the presence of small polyhedra being compensated by large supercages. While we believe that none is feasible in a traditional zeolite or AIPO composition, they may be of interest in several areas of chemistry, for instance if it were possible to form the D3R unit as a precursor. All the structures are cubic and have at least  $m\bar{3}m$  symmetry. Structure 2\_43 (Figs. 8d–f) is the most feasible ( $\vartheta = 11.62$ ) and has D3R units attached to  $[3^46^4]$  truncated tetrahedra to form tetrahedral units (Fig. 8e). ‘Truncated cube’ cages are present, as are the large  $[4^{24}6^88^{18}]$  cages shown in Fig. 8(f). In 2\_64 the D3R are also attached to truncated cube cages, but the structure additionally

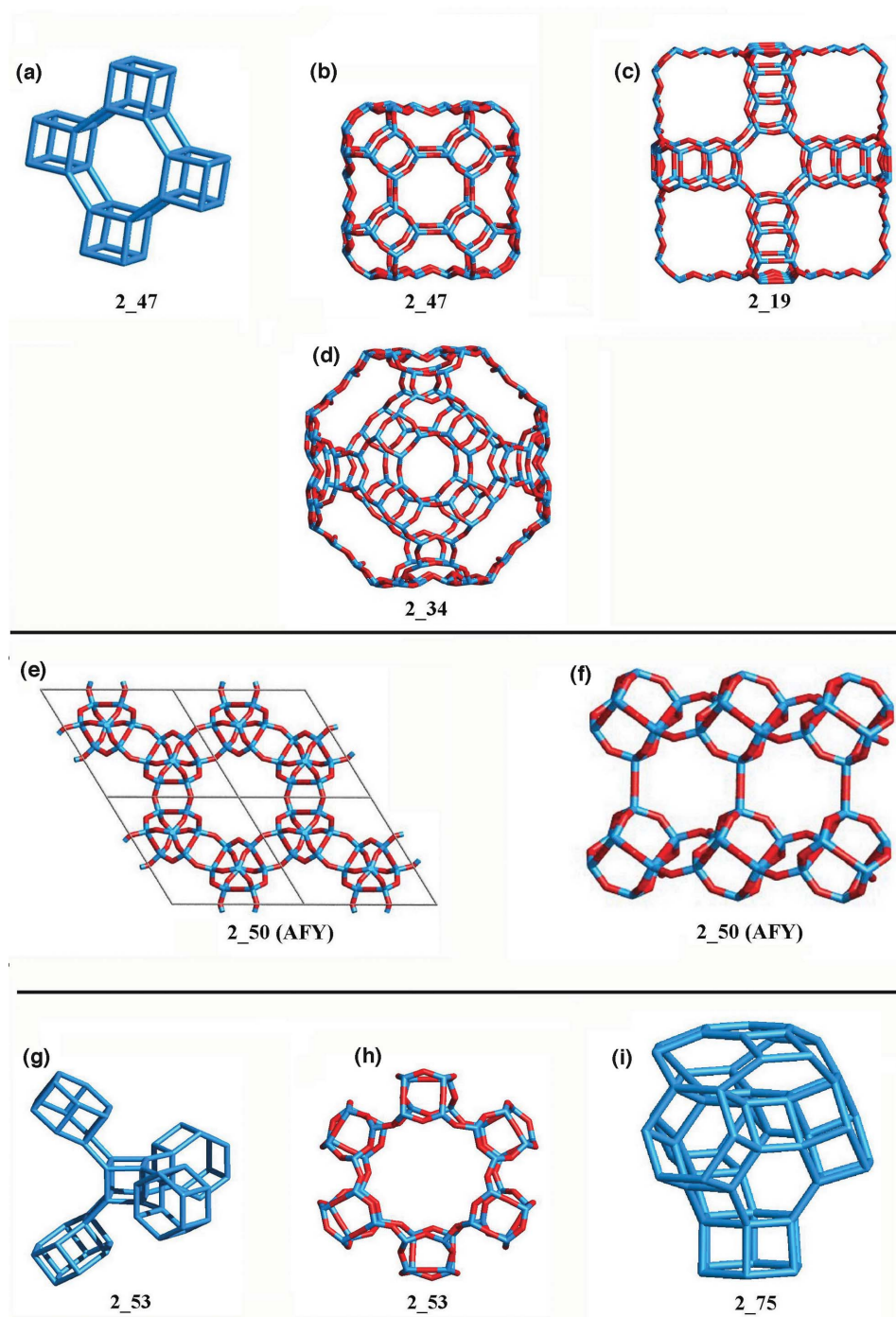
contains alpha and  $[4^{24}6^88^{18}]$  tshörtnerite (TSC) cages. Structure 2\_23 has beta cages linked *via* D3R–four-ring–D3R bridging units and 2\_26 also has the same unit of two D3R linked through a four-ring (as do 2\_25 and 2\_22), with alpha cages present. Structure 2\_25 has a pore system connected through 12-ring apertures and contains, besides FAU super-cages and LTA alpha cages, the large  $[4^{24}8^612^8]$  cages found in the RWY structure. Structure 2\_41 is similar to 2\_43, as the

D3R form an alternating network with truncated tetrahedra (as in Fig. 8e). Structure 2\_22 is also of very low density ( $F_D = 9.70 T$  per  $1000 \text{ \AA}^3$ ) and has the D3R connected so as to define D8R. Finally, 2\_4 and 2\_8 are among the least dense of all the binodal simple tile structures, with  $F_D$  of 5.39 and 6.48  $T$  per  $1000 \text{ \AA}^3$ , respectively. The basic building unit of 2\_8 is two D3R stacked with an intervening D4R (Fig. 8g). In 2\_4 the intermediate unit is absent and D3R units join directly through a shared four-ring. In both cases, very open cavity systems are constructed by connection of these units (Fig. 8h).

both cases, very open cavity systems are constructed by connection of these units (Fig. 8h).

### 3.13. Three-ring family

This family of eight structures is characterized by the presence of three-rings. Five structures contain pairs, or longer chains, of three-rings which share one  $T$  atom and therefore contain the spiro-5 unit (Baerlocher *et al.*, 2001). Two of the structures also contain four-rings. As expected, several of the structures are of low density, but none would be expected to be realisable as a conventional zeolite. In 2\_71, the most feasible with  $\vartheta = 17.07$ , three-rings themselves form rings of six (Fig. 8i), with the structure also containing elongated cages having eight-rings as their largest pore. The basic unit of 2\_69 is a pair of edge-sharing three-rings (or bridged four-ring, Fig. 8j). These larger units then connect to define a hexagonal channel system. Structure 2\_65 also contains loops of six three-rings, virtually identical in structure to those in 2\_71. However, the structure is much more open ( $F_D = 12.28$ , compared with 17.38 for 2\_71), containing a three-dimensional network of 10- and 12-ring pores. Structure 2\_44 is another very open structure ( $F_D = 10.36$ ), with a three-dimensional network of corner-sharing three-rings defining the small  $[3^46^4]$  cages shown in Fig. 8(k), as well as large cavities linked through 12-rings. Structure 2\_12 has unusual chains built up from pairs of edge-sharing three-rings and has large cross-linked channels extending in two dimensions, delineated by puckered 14-membered rings (Fig. 8l). Structure 2\_29 is an



**Figure 7**

Molecular graphic illustrations of some structures from the D8R family, AFY structures and the D6R family.

unusually complex cubic structure, with three- and four-rings linked together (Fig. 8*m*): pairs of edge-sharing three-rings are formed (there are no spiro-5 units) and these pairs are further connected by distorted four-rings. Uniquely for this family, in 2\_105 the three-rings do not directly link into chains or pairs through the sharing of *T* atoms, but rather connect through oxygen bridges to define five-rings. Finally, 2\_9 has H-shaped building units in which four-rings share edges with pairs of three-rings (Fig. 8*n*).

### 3.14. [3<sup>4</sup>] family

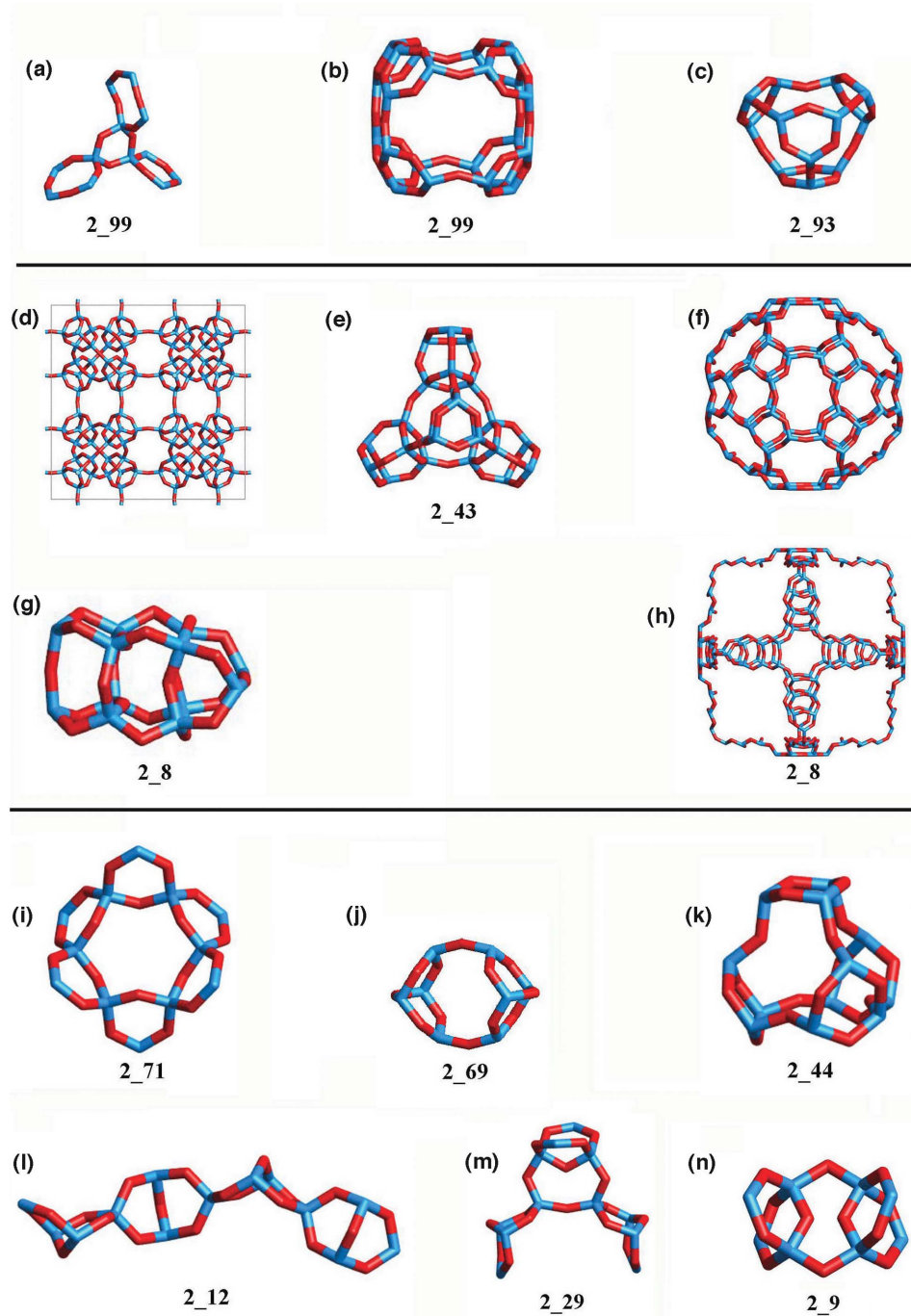
The common feature of this family is a [3<sup>4</sup>] unit, sometimes known as the ‘supertetrahedron’ or ‘tetrahedron of tetrahedra’. This unit is unknown in zeolitic oxide materials, but is present in some sulfides, including the zeotypic RWY structure and the compound Na<sub>2</sub>Si<sub>2</sub>S<sub>5</sub>. Structure 2\_16 (Figs. 9*a* and *b*), one of the few structures containing seven-rings, is characterized by its [3<sup>8</sup>4<sup>2</sup>7<sup>8</sup>8<sup>4</sup>] cage (Fig. 9*b*). Each of the eight three-rings forms part of a [3<sup>4</sup>] unit, shared with three other cages. This structure is the most feasible of this family, with  $\vartheta = 36.19$ . Similarly, 2\_14 has only one type of ‘larger’ cage, [3<sup>8</sup>4<sup>2</sup>6<sup>4</sup>8<sup>8</sup>], and the whole structure can be thought of in terms of the sodalite framework, but with one third of the *T* sites replaced by [3<sup>4</sup>] supertetrahedra. Structure 2\_15 is also related to the sodalite structure, although now with half of the original *T* sites replaced by the [3<sup>4</sup>] units, creating [3<sup>12</sup>6<sup>6</sup>9<sup>8</sup>] cages. Structure 2\_10 can be derived from the RHO zeolite structure by replacement of all *T* sites by [3<sup>4</sup>] tetrahedra. As a result, it possesses very large cages linked *via* double 16-membered rings (Fig. 9*c*). Finally, structure 2\_7, being the least dense of this family ( $F_D = 8.60$ ), has [3<sup>4</sup>6<sup>4</sup>] units (‘truncated tetrahedra’) linked *via* chains of four-rings and [3<sup>4</sup>] units (Fig. 9*d*). This very open cubic structure has 16-MR pores in all three dimensions.

### 3.15. Orphan structures

We show three selected structures out of the 12 which cannot be categorized in our ‘family’ system.

Structure 2\_96, a feasible zeolite structure ( $\vartheta = 5.45$ ), is unusual as it contains small [4<sup>3</sup>5<sup>2</sup>6<sup>2</sup>] cage units (Fig. 9*e*) interconnected through shared four-rings to form a three-dimensional network (Fig. 9*f*), thereby defining the [5<sup>12</sup>6<sup>20</sup>] cage which also appears in structure 2\_97.

Structure 2\_37 (Figs. 9*h–j*): the basic building unit is the D4R, which links *via* four-rings to create double 12-membered rings (Fig. 9*i*), which are in turn linked into



**Figure 8**  
Molecular graphic illustrations of structures from the three- and four-ring family, the D3R family and the three-ring family.

large  $[4^36^412^8]$  supercages with tetrahedral symmetry, with four puckered 12-rings and four 12-rings which are almost planar (Fig. 9j). This cubic structure is quite open with  $F_D = 12.58 T$  per  $1000 \text{ \AA}^3$ , but is of intermediate feasibility ( $\vartheta = 18.50$ ).

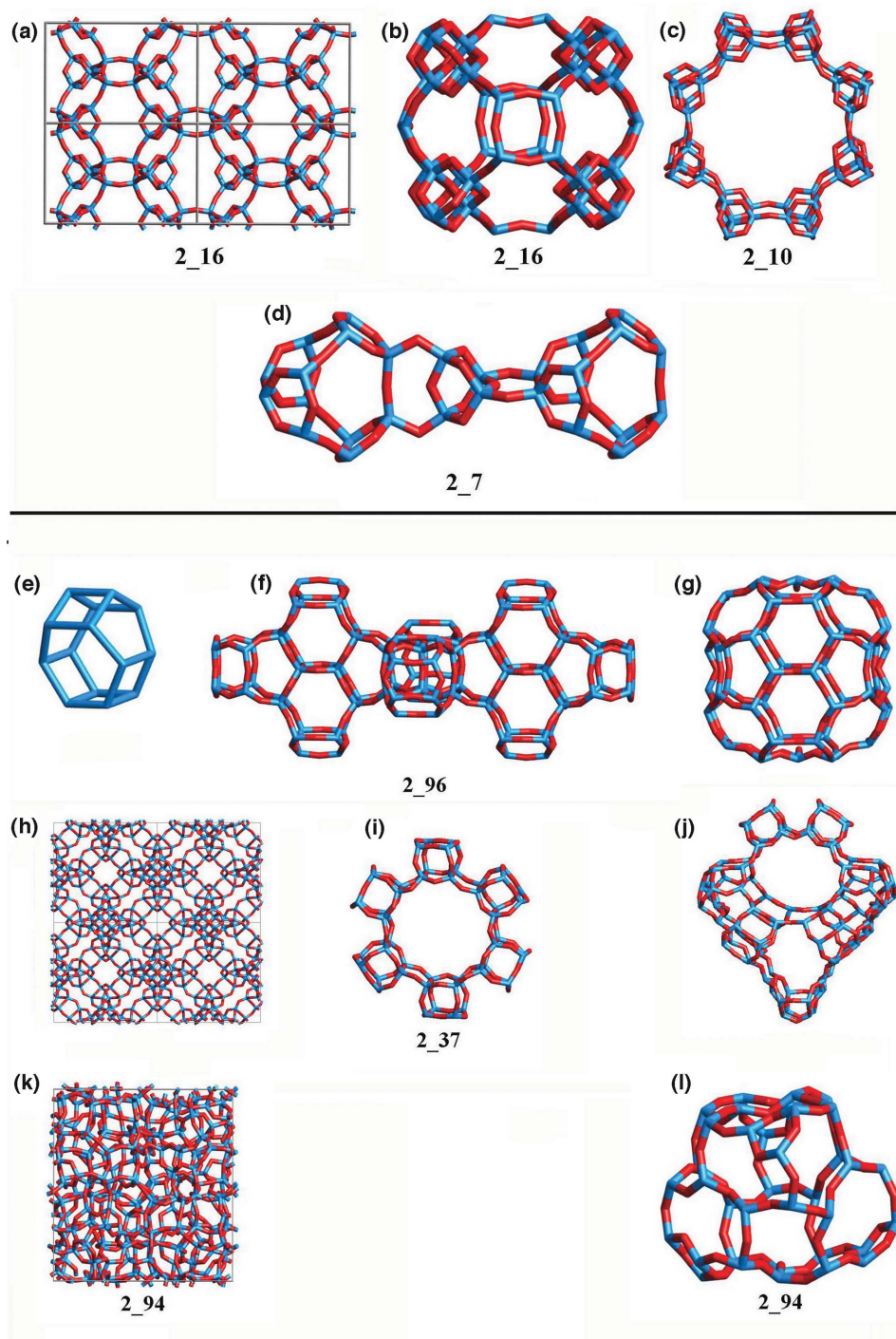
Structure 2\_94 (Figs. 9k and l) contains  $[3^46^4]$  truncated tetrahedra, distorted sodalite cages, and larger cages with three- and six-rings (Fig. 9l). The ideal symmetry of the structure is  $Fd\bar{3}m$ . However, in silica form it appears highly

strained in this symmetry, preferring to minimize in space group  $C2$ , giving rise to its somewhat distorted appearance.

#### 4. Conclusions

We have evaluated and characterized 109 hypothetical zeolite structures, of which 98 do not correspond to known zeolite frameworks. Among these are many promising candidates for zeolite synthesis. Some of the most

feasible as conventional aluminosilicates or AlPOs are those in the ABC-6 family, composed principally of four- and six-rings, although from the point of view of porosity, the more likely structures will be at best small-pore zeolites, having no aperture larger than the eight-ring. Other promising candidates come from structures which similarly have features in common with known zeolites, such as those in the AWW and SAS families (Figs. 5 and 6), where cages stack through shared eight-rings. Again, four- and six-rings predominate, with the eight-ring being the limiting aperture in all cases, as it is for the more feasible structures in the  $[4^25^6]$  family. At the other end of the scale, many very open structures also exist. These illustrate well the principle (Brunner & Meier, 1989) that less dense structures require a greater proportion of small (three- or four-membered) rings. Here, we can extend this to state that larger cavities also require the presence of much smaller cages. Hence, we find large-pore structures containing  $[3^4]$  units (Fig. 9), double three-rings (Fig. 8) and three-rings, as well as pairs and chains of three- and four-rings. In terms of aluminosilicate and aluminophosphate zeolites, these structural units, particularly those containing three-rings, are by and large disfavoured due to the strain imposed on the  $\text{TO}_4$  tetrahedra. In fact, it is apparent that feasibility decreases markedly as more three-rings are connected together with, for example, structures containing  $[3^4]$  units having higher values than those containing only spiro-5 units. The most viable



**Figure 9** Molecular graphic illustrations of structures from the  $[3^4]$  family and of some of the orphan structures.



three-ring structures are those in which the three-rings are isolated from one another. The best example is 2\_103 which contains the  $[3^25^6]$  unit (Fig. 4g), reminiscent of the  $[3^14^35^3]$  units in the MEI structure. Structure 2\_103 is the most feasible large-pore zeolite among our 109 structures. Similarly, although four-rings are found in the most feasible structures, agglomerations of these units, obtained by stacking prismatic units such as D4R and D6R, result in decreasing likelihood (although individual D4R and D6R are tolerated, unlike D3R).

Having discounted many of the more open structures as potential zeolites on account of the presence of these small units, we do not exclude the possibility that these topologies could be possible in other chemical compositions where the local coordination environments are less constrained. Indeed, if we could construct units such as the D3R or the super-tetrahedron as precursor species, many open framework architectures could be synthesized.

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## References

- Akporiaye, D. E. & Price, G. D. (1989). *Zeolites*, **9**, 23–32.
- Alberti, A. (1979). *Am. Mineral.* **64**, 1188–1198.
- Baerlocher, C. & McCusker, L. B. (2004). <http://www.iza-structure.org/databases>.
- Baerlocher, C., Meier, W. M. & Olson, D. H. (2001). *Atlas of Zeolite Structure Types* (updates at <http://www.iza-structure.org/>), 5th ed. London: Elsevier.
- Barrer, R. M. & Villiger, H. (1969). *Z. Kristallogr.* **128**, 352–370.
- Bialek, R. (1995). *KRIBER*, Version 1.1. Institut für Kristallographie und Petrographie, ETH, Zürich, Switzerland.
- Boisen, M. B., Gibbs, G. V., O'Keeffe, M. & Bartelmehs, K. L. (1999). *Micropor. Mesopor. Mater.* **29**, 219–266.
- Brunner, G. O. & Meier, W. M. (1989). *Nature*, **337**, 146–147.
- Connolly, M. L. (1985). *J. Am. Chem. Soc.* **107**, 1118–1124.
- Delgado Friedrichs, O. (2001). *Discret. Comput. Geom.* **26**, 549–571.
- Delgado Friedrichs, O., Dress, A. W. M., Huson, D. H., Klinowski, J. & Mackay, A. L. (1999). *Nature*, **400**, 644–647.
- Dress, A. W. M., Huson, D. H. & Molnár, E. (1993). *Acta Cryst.* **A49**, 806–817.
- Foster, M. D., Bell, R. G. & Klinowski, J. (2001). *Stud. Surf. Sci. Catal.* **136**, 266.
- Foster, M. D., Delgado Friedrichs, O., Bell, R. G., Almeida Paz, F. A. & Klinowski, J. (2003). *Angew. Chem. Int. Ed.* **42**, 3896–3899.
- Foster, M. D., Friedrichs, O. D., Bell, R. G., Almeida Paz, F. A. & Klinowski, J. J. (2004). *Am. Chem. Soc.* **126**, 9769–9775.
- Foster, M. D., Simperler, A., Bell, R. G., Delgado Friedrichs, O., Almeida Paz, F. A. & Klinowski, J. (2004). *Nature Mater.* **3**, 234–238.
- Foster, M. D. & Treacy, M. M. J. (2004). *Hypothetical Zeolites: Enumeration Research*; <http://www.hypotheticalzeolites.net/> 2004.
- Henson, N. J., Cheetham, A. K. & Gale, J. D. (1994). *Chem. Mater.* **6**, 1647–1650.
- Hu, Y. T., Navrotsky, A., Chen, C. Y. & Davis, M. E. (1995). *Chem. Mater.* **7**, 1816–1823.
- Klinowski, J. (1998). *Curr. Opin. Solid State Mater. Sci.* **3**, 79–85.
- Koningsveld, H. van (2004). *Schemes for Building Zeolite Structure Models*, in *Database of Zeolite Structures*; <http://topaz.ethz.ch/IZA-SC/ModelBuilding.htm>.
- Liebau, F., Gies, H., Gunawardane, R. P. & Marler, B. (1986). *Zeolites*, **6**, 373–377.
- Meier, W. M. (1986). *Zeolites and Zeolite-Like Materials*. 7th Int. Zeolite Conference, Tokyo, 17–22 August.
- Meier, W. M. & Villiger, H. (1969). *Z. Kristallogr.* **128**, 352–370.
- Mellot-Draznieks, C., Girard, S., Férey, G., Schön, J. C., Cancarevic, Z. & Jansen, M. (2002). *Chem. Eur. J.* **8**, 4103–4113.
- Mellot-Draznieks, C., Newsam, J. M., Gorman, A. M., Freeman, C. M. & Férey, G. (2000). *Angew. Chem. Int. Ed.* **39**, 2270–2275.
- Molecular Simulations Inc. (1999). *Cerius<sup>2</sup>*, Version 4.0. Molecular Simulations Inc., San Diego, USA.
- Moloy, E. C., Davila, L. P., Shackelford, J. F. & Navrotsky, A. (2002). *Micropor. Mesopor. Mater.* **54**, 1–13.
- O'Keeffe, M. & Hyde, S. T. (1996a). *Z. Kristallogr.* **211**, 73–78.
- O'Keeffe, M. & Hyde, B. G. (1996b). *Crystal Structures I: Patterns and Symmetry*. Mineralogical Association of America Monograph, Washington, DC.
- Navrotsky, A., Petrovic, I., Hu, Y. T., Chen, C.-Y. & Davis, M. E. (1995). *Micropor. Mater.* **4**, 95–98.
- Persistence of Vision Raytracer Pty. Ltd (2004). *POV-Ray*, Version 3.6. Persistence of Vision Raytracer Pty Ltd.
- Petrovic, I., Navrotsky, A., Davis, M. E., Zones, S. I. (1993). *Chem. Mater.* **5**, 1805–1813.
- Piccione, P. M., Laberty, C., Yang, S. Y., Cambor, M. A., Navrotsky, A. & Davis, M. E. (2000). *J. Phys. Chem. B*, **104**, 10001–10011.
- Piccione, P. M., Woodfield, B. F., Boerio-Goates, J., Navrotsky, A. & Davis, M. E. (2001). *J. Phys. Chem. B*, **105**, 6025–6030.
- Piccione, P. M., Yang, S. Y., Navrotsky, A. & Davis, M. E. (2002). *J. Phys. Chem. B*, **106**, 3629–3638.
- Sastre, G. & Gale, J. D. (2001). *Micropor. Mesopor. Mater.* **43**, 27–40.
- Sato, M. (1984). *Framework Topology and Systematic Derivation of Zeolite Structures*, edited by D. H. Olson and A. Bisio. In Proc. of the 6th Intl Zeolite Conference, Reno, USA, 10–15 July. Guildford: Butterworths.
- Sato, M. J. (1987). *Phys. Chem.* **91**, 4675–4681.
- Sherman, J. D. & Bennett, J. M. (1973). *Molecular Sieves*, edited by W. M. Meier and J. B. Uytterhoeven, Vol. 121, p. 52. Washington, DC: American Chemical Society.
- Simperler, A., Foster, M. D., Bell, R. G. & Klinowski, J. (2004). *J. Phys. Chem. B*, **108**, 869–879.
- Smith, J. V. (1988). *Chem. Rev.* **88**, 149–182.
- Smith, J. V. (1993). *ACS Abstr.* **205**, 157-IEC.
- SourceForge (2004). *GDIS*, Version 0.84. SourceForge.
- Treacy, M. M. J., Randall, K. H., Rao, S., Perry, J. A. & Chadi, D. J. (1997). *Z. Kristallogr.* **212**, 768.
- Wells, A. F. (1977). *Three-Dimensional Nets and Polyhedra*. New York: Wiley.
- Wells, A. F. (1979). *Further Studies of Three-Dimensional Nets*, American Crystallographic Association Monograph No. 8, Vol. 9. Pittsburgh, PA: Polycrystal Book Service.
- Wells, A. F. (1984). *Structural Inorganic Chemistry*, 5th ed. Oxford University Press.