Potential zeolites related to faujasite (FAU): structures and energetics.

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Abstract

We describe five new zeolitic framework types, **fav**, **faw**, **fax**, **fay** and **sod-t** that are structurally related to faujasite. They are derived from isomorphic expansions of the tetrahedral nets associated with selected Frank-Kasper phases. Each tetrahedral vertex of the net is replaced by a sodalite cage (S) and each edge by a hexagonal prism (P), in effect replacing each vertex with an SP_4 tetrahedron. Faujasite itself, framework type **FAU**, is an SP_4 expansion of the diamond net.

In the Frank-Kasper phases the periodic incorporation of icosahedra, which can be subdivided into twenty almost-regular tetrahedral volumes, tends to minimize distortion of the associated tetrahedral SP_4 framework, ensuring low framework energies. The computed framework energy of silicate **fav** compares most favorably with that for **FAU** and **EMT**, presenting an appealing zeolite synthesis target.

1. Introduction, terminology and definitions

Zeolites with the faujasite framework are among the most valuable of inorganic materials in the economic sense. In this paper we explore related framework structures that are potential targets for synthesis and which might be equally valuable materials. We start with some definitions and terminology necessary for understanding the provenance of these new structures.

A *simple* polyhedron is one in which exactly two faces meet at each edge and three meet at each vertex. A *simple* tiling is a tiling of space by simple polyhedra in which exactly two polyhedra meet at each face, three at each edge and four at each vertex. Foams are simple tilings; so are the frameworks of many important zeolites.

In a 3-dimensional tiling there is a dual tiling generated as follows. Place a new vertex in each old tile, connect these through faces to the new vertices in adjacent tiles. Now recognizing that the dual of a dual is the original tiling, the old vertices are in the new (dual) tiles and the old edges pass through the new faces. For our purpose we note that the dual of a simple tiling is a tiling by tetrahedra and vice versa.

The set of edges and vertices of a tiling (the *1-skeleton*) form a net. Nets of interest in structural chemistry are assigned a three-letter (bold, lower-case) RCSR code **xyz**.[1] If it is the approved net of a known zeolite it is assigned an IUPAC (bold, upper-case) code **XYZ** by the Structure Commission of the International Zeolite Association.[2] In the case of faujasite the zeolite framework type code is **FAU**. In RCSR the same net is identified as **fau**.

We are concerned here with the linking of groups with tetrahedral shape in which the linkage is either *staggered* with an inversion center between the two groups, or *eclipsed* with a (local) mirror between the two parts. Specifically, linking vertices with four edges and linking truncated octahedra with hexagonal-prism edges, with minimal torsional stress, as shown in Figure 1.

In the approach to tiling by the Dress group [3, 4] tiles are split into tetrahedral *chambers* in which the vertices are at a vertex of the tile, in the center of an adjacent edge, in the center of an adjacent face and in the center of the tile. The set of chambers of the tiling form a tiling by tetrahedra. The dual of this tiling is a simple tiling with a net we call the "**-t** net". These are useful for studying the periodic surfaces associated with a net.[5] For the present purpose we note that if the original tiling is simple, in the zeolitic form of the **-t** structure the SiO_4 tetrahedra (with Si at the vertices and O on the edges) are replaced by truncated octahedra (sodalite cages, S) and the edges (O atoms) replaced by hexagonal prisms (P) to form SP_4 units (Fig. 1). This is exactly what we want to find structures related to **FAU**. Note that the number of different (unrelated by symmetry) chambers, *D*, in the tiling is the *flag transitivity* and is reported as *D size* in RCSR (*D* from Delaney-Dress-Delgado symbol). It follows that a **-t** net is vertex *D*-transitive.

The next question is which nets to select to make viable **FAU**-related structures. Linking tetrahedral vertices in all-staggered conformation leads inexorably to the diamond net (**dia**). Staggered linking of truncated octahedra with trigonal prisms similarly produces the **FAU** framework (Figure 2).

A "cousin" of **FAU**, namely **EMT**, is known as a zeolite (Figure 3). This has the lonsdaleite (**lon**) underlying net, which can be augmented with SP_4 units, preserving the local tetrahedral symmetry of the truncated octahedron and four joined hexagon prisms. Only one quarter of the junctions are in the eclipsed conformation but there is no intrinsic stress penalty introduced by this eclipsed versus staggered packing.

Linking in an all-staggered conformation is not possible with strictly regular conformation, but it can be shown readily[6, 7] that, with a small deformation, five such groups can be linked to form a low-stress pentagon (the angle in a regular pentagon is 108˚ whereas the tetrahedral angle is 109.47˚). Ideally, to continue further the assembly would form a simple tiling by tiles with pentagonal faces. However, a tiling by pentagonal dodecahedra fits on the 3-sphere and to make a simple tiling in flat 3D space, 6-rings are inevitable. In terms of the dual structure it is noted that tilings by tetrahedra in which five tetrahedra meet at every edge is impossible, and there must be some edges where six tetrahedra meet. Such structures are the basis for the celebrated Frank-Kasper intermetallic compounds.[8, 9] It has been shown rigorously that there are just two simple possibilities that are tile 3-transitive.[10] These correspond to the $MgCu_2$ and Cr_3Si Frank-Kasper phases. Relevant to our discussion is the fact that the dual simple structures are those of the zeolite frameworks **MTN** and **MEP** respectively. The fraction of 6-rings is smallest in **MTN** (1/10 compared to 1/9 for **MEP**). The augmented **-t** nets corresponding to these two (Figure 4) have symbols **fav** ("**mtn-t**", vertex transitivity 17) and **faw** ("**mep-t**", vertex transitivity 23).

A related common intermetallic structure based on packing tetrahedra is the extended (14-coordinated) body-centered cubic **bcu-x**. In this structure either four or six tetrahedra meet at an edge. The dual structure is the familiar sodalite (**SOD**) framework constructed of polyhedra with 4- and 6-rings. The absence of 5-rings suggests that, after expansion, the SP_4 tetrahedral groups will be more strained. For comparison, we include this **-t** net SP_4 expansion, **sod-t** (vertex transitivity 3), as a **FAU** analog (Figure 5).

2. Framework energy calculations

Upon close inspection (Figure 4, and Tables 2–4), the **fav** (symmetry $Fd\overline{3}m$), **faw** (symmetry $Pm\overline{3}n$), and **sod-t** (symmetry $Im\overline{3}m$), structures exhibit small, but discernible, deformations to the sodalite and double 6-ring cages, suggesting that the silicate framework energies may be higher than the relatively unstrained **FAU** and **EMT** frameworks. To explore this energetic penalty, the frameworks were relaxed at constant pressure conditions by the General Utility Lattice Program (GULP)[11, 12] using the Sanders-Leslie-Catlow potential[13] for SiO_2, and the results are presented in

Table 1. To five significant figures the **fav** framework has framework energy -128.45 eV/SiO_2, slightly higher than that for **FAU** and **EMT** **(**-128.50 eV/SiO_2**)**. The **faw** framework has higher energy, -128.38 eV/SiO_2, and the **sod-t** energy of -128.33 eV/SiO_2 is higher yet. For comparison, the quartz framework is -128.64 eV/SiO_2. These energies fall within the normal range for many known zeolites when modeled as silicates.[14] Compared to **FAU** and **EMT**, GULP reported that **fav** and **faw** exhibited stronger core-shell polarization of some oxygen atoms. Further, in full symmetry, phonon modes with negative eigenvalues, ω^2, occurred, suggesting that the structures are metastable and may be more stable under a lower symmetry, or possibly with mixed composition, such as an alumino- or germano-silicate. Negative eigenvalues arise for a number of normal zeolite structures, one example being **MTN** itself, and do not necessarily disqualify a framework from the realms of plausibility. We did not explore these avenues further.

We note in passing that the framework of zeolite tschörtnerite, **TSC**, is also built from SP_4 units, but it is not an SP_4 augmentation of a **-t** net, as investigated here: the double 6-ring prisms (P) in **TSC** do not correspond to edges of a **-t** net. SP_4-augmented **-t** nets will have, on average, two hexagonal prisms to each sodalite, for a "composition" of SP_2, but the "composition" of **TSC** is SP_4. Nevertheless, it is worth noting that the framework energy of **TSC** is -128.50 eV/SiO_2, comparable to **FAU** and **EMT**, indicating that the SP_4 units are minimally stressed in **TSC**.

We note that **fav,** which is built on the **MTN** framework with the most 5-rings (9 out 10), has a more favorable energy than **faw**, which is built on the **MEP** framework with lightly fewer 5-rings (8 out of 9). **sod-t**, based on the **SOD** framework with no 5-rings has even higher energy, as expected. Comparison of framework energies of **FAU** and **EMT** confirms there is no intrinsic penalty for the eclipsed configuration of the SP_4 units.

3. Descriptions of the structures

The tiles of the "parent" structures define cages (e.g. the adamantane cage in the **dia** structure, shown in Fig. 6). In the **FAU**-related family, we have described the vertices of the parent net as being replaced by a truncated octahedron, and the edges by hexagonal prisms (forming the SP_4 unit). Alternatively, we can describe the transformation as replacing the vertices of the *tiles* by a hexagonal prism of vertices. Thus, the adamantane cage of **dia** transforms into the faujasite cage of **FAU** (Fig. 2). The generation of the cages in **sod-t**, **fav**, and **faw** is shown in Fig. 6. Note that

mtn and **mtp** have two tiles each, one of which is the pentagonal dodecahedron. The corresponding cage in **fav** and **faw** is the 120-vertex Archimedean polyhedron **ild** with icosahedral symmetry.

The tile in **SOD** (the parent of **sod-t**) is a truncated octahedron (**tro** in RCSR); in **sod-t** it becomes the polyhedron (**tro-e-a**) with 144 vertices (Fig 6). **MTN** and **MEP** (parents of **fav** and **faw**) each contain two kinds of tile. In **MTN** they are two dodecahedra [5^{12}] and one hexakaidecahedron [$5^{12}.6^4$]. In **MEP** the tiles are one dodecahedron [5^{12}] and three tetrakaidecahedra [$5^{12}.6^2$]. Noteworthy is that the cage derived from the dodecahedron has icosahedral symmetry and is the largest Archimedean polyhedron – the truncated icosidodecahedron (**tid**).

The GULP-refined coordinates for **fav**, **faw** and **sod-t** are given in tables 2, 3 and 4 respectively.

4. Discussion and Conclusions

It is tempting to infer that every regular-tetrahedral (zeolitic) net can be subjected to such an isomorphic transformation by augmenting vertices of the **-t** net with SP_4 units. However, most zeolitic nets augmented this way will strain the SP_4 units, raising the framework energy above the bounds of feasibility. In a silicate SiO_4 tetrahedron, for example, the Si–O–Si angles tend to be in the range 140° to <180°. However, the S–P–S angle is constrained to be near 180°. Thus, the existence of a viable silicate net does not ensure a viable SP_4 augmentation. As we show here, two exceptions are the **MTN** and **MEP** frameworks, which are based on the simplest Frank-Kasper phases. The key is that these frameworks are rich in regular 5-rings, with angles of 108° between edges, which closely matches the tetrahedral angle of 109.47° favored by the ideal **-t** net, while allowing S–P–S angles to be close to 180°. Consistent with the fact that **MTN** has a slightly higher 5-ring to 6-ring ratio than does **MEP**, 9/1 and 8/1 respectively, the **fav** (**mtn-t**) structure has a lower framework energy (less distortion) than the **faw** (**mep-t**) structure. **SOD** itself, having no 5-rings, has more framework distortion and a concomitant higher framework energy.

The low energies of **fav** and **faw** lead us to ask if other **-t** nets derived from Frank-Kasper phase duals would be suitable candidates. The next-simple structure is that of the Zr_4Al_3 type, the dual of which is the clathrate variously known as type II or type IV (RCSR symbol **isq**). The tiling has *D*-size = 40 implying that the **-t** net is vertex 40-transitive. However, the plausibly-low framework energy for **sod-t** suggests that isolated (not edge-sharing) 4-rings might not impose too large an energy, so a search was made in RCSR for clathrates with *D*-size <30. This led to two more candidate structures. The first, **alb-x-d** (*D*-size = 16), is the dual of the AlB_2 net, which is another intermetallic structure based on tetrahedron packing.[15] The simple tiling is a packing of enneahedra [$4^3.5^6$] and icosahedra [$5^{12}.6^8$] ("hexagonal barrels"). The corresponding **-t** net has been assigned the symbol **fax**. The GULP energy of this, as an SiO_2 framework, is -128.26 eV/SiO_2, which, although higher than **FAU**, is still plausible. Aspects of the structure are depicted in Fig. 7 and the coordinates are given in Table 5. Note the large cage, which suggests that synthesis might be effected with the aid of a large structure-directing template.

The other simple tiling from the RCSR search, **isq**, is an isohedral tiling first described many years ago.[16, 17] This has *D*-size 18 and yields a **-t** net assigned symbol **fay**. The framework energy is -128.22 eV/SiO_2, which is the highest framework energy of the structures studied here. The structure is shown in Fig. 8, and the coordinates are given in Table 6.

The energetic plausibility of the **fav** framework, and possibly the **faw** and **sod-t** frameworks, which are closely related to the **FAU** framework, presents an interesting synthetic challenge to the zeolite community. This challenge is not dissimilar to the possibilities raised by Breck[18] when he conjectured on the possibility of the hypothetical 'Structure 6', or 'hexagonal faujasite', which was later successfully synthesized as the framework type **EMT**.[19]

We note also, relevant in this context, the design and successful synthesis of large cubic zeolites based on the building units of the **RHO** structure.[20, 21]

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Table 1: Framework energies, U, per SiO_2 for SP_4-based zeolites computed using the Sanders-Leslie-Catlow silica empirical potential in GULP. The energy for quartz, **qtz**, is added for comparison. The energies are all within the range of the known zeolites when modeled as silicates. The diameter of the largest included sphere, D_i, and of the largest freesphere, D_f, indicate the cavity size and relative porosity of the structures.

Code	U (eV)	D_i (Å)	D_f (Å)
qtz	−128.640	1.86	1.45
TSC	−128.502	16.05	4.01
FAU	−128.498	10.99	7.17
EMT	−128.495	11.33	7.17
fav	−128.451	23.49	7.73
faw	−128.379	19.88	6.56
sod-t	−128.333	20.38	7.61
fax	−128.260	25.40	7.03
fay	−128.218	13.88	7.00

Table 2. Atomic coordinates for the **fav** (**mtn-t**) framework, optimized as a silicate by GULP in cubic space group $Fd\overline{3}m$, with $a = 64.696$ Å.

Atom	x	y	z
Si1	0.09180	0.12450	0.55828
Si2	0.23781	0.30396	0.33798
Si3	0.28147	0.31496	0.34867
Si4	0.22700	0.25977	0.32482
Si5	0.00306	0.03598	0.28090
Si6	0.02085	0.16699	0.43252
Si7	0.03420	0.12513	0.36624
Si8	0.07720	0.10991	0.37552
Si9	0.04803	0.13989	0.32290
Si10	0.09161	0.12428	0.33221
Si11	0.06426	0.15129	0.44395
Si12	0.09157	0.12384	0.41906
Si13	0.16974	0.25656	0.28993
Si14	0.00827	0.12204	0.30532
Si15	0.00607	0.15177	0.39188
Si16	0.00561	0.21110	0.33529
Si17	0.03341	0.18336	0.30795
O1	0.10415	0.10415	0.55132
O2	0.10723	0.14277	0.56482
O3	0.07810	0.11925	0.57810
O4	0.07776	0.13136	0.53895
O5	0.21796	0.30868	0.35223
O6	0.25748	0.30980	0.35187
O7	0.23939	0.28033	0.33080
O8	0.23662	0.31714	0.31714
O9	0.29382	0.29382	0.34625
O10	0.28530	0.32793	0.32793
O11	0.22408	0.25909	0.30015
O12	0.20474	0.26000	0.33594
O13	0.23993	0.23993	0.33265

Atom	x	y	z
O14	0.02511	0.02511	0.27747
O15	0.98915	0.03250	0.26085
O16	0.00755	0.06028	0.28475
O17	0.00724	0.15417	0.41645
O18	0.02127	0.19082	0.42544
O19	0.04405	0.15862	0.43183
O20	0.04160	0.13869	0.34683
O21	0.01453	0.11108	0.36141
O22	0.05232	0.10968	0.37379
O23	0.02707	0.14102	0.38394
O24	0.08653	0.08653	0.37601
O25	0.08686	0.12246	0.35647
O26	0.08305	0.12231	0.39597
O27	0.04669	0.16383	0.31603
O28	0.07067	0.12962	0.31956
O29	0.03236	0.12656	0.30906
O30	0.08101	0.16899	0.44104
O31	0.07295	0.12976	0.43464
O32	0.10218	0.10218	0.42611
O33	0.10844	0.14156	0.41925
O34	0.16401	0.27092	0.27092
O35	0.14987	0.24221	0.29360
O36	0.99771	0.14027	0.29215
O37	0.99577	0.12044	0.32672
O38	0.01643	0.23357	0.33168
O39	0.02077	0.19307	0.32712
O40	0.98336	0.20964	0.32344
O41	0.04956	0.20044	0.29892
O42	0.10671	0.14329	0.32871
O43	0.10296	0.10296	0.32450

Table 3. Atomic coordinates for the **faw** (**mep-t**) framework, optimized as a silicate by GULP in cubic space group $Pm\overline{3}n$, with $a = 44.941$ Å.

Atom	x	y	z	Atom	x	y	z
Si1	0.03387	0.41426	0.25055	O16	0.10203	0.23231	0.22270
Si2	0.03387	0.35996	0.21005	O17	0.05998	0.22134	0.21298
Si3	0.06521	0.30029	0.20322	O18	0.08664	0.18763	0.19291
Si4	0.20050	0.20388	0.28557	O19	0.09151	0.21594	0.09744
Si5	0.06534	0.23531	0.08808	O20	0.08043	0.26564	0.08802
Si6	0.08609	0.20243	0.22337	O21	0.04961	0.24817	0.06098
Si7	0.10717	0.14771	0.25728	O22	0.04961	0.22238	0.11516
Si8	0.17608	0.26014	0.25680	O23	0.13687	0.14655	0.27353
Si9	0.09259	0.32778	0.14769	O24	0.10699	0.13269	0.22692
Si10	0.08795	0.09552	0.29596	O25	0.09756	0.12162	0.27662
Si11	0.03388	0.20945	0.14223	O26	0.14703	0.26117	0.23942
Si12	0.10680	0.11767	0.19656	O27	0.09406	0.31187	0.11782
Si13	0.03387	0.24024	0.20258	O28	0.11899	0.30878	0.15713
Si14	0.14539	0.28978	0.16667	O29	0.07572	0.35704	0.15027
Si15	0.11797	0.26219	0.22203	O30	0.06091	0.07972	0.30886
Si16	0.08718	0.17283	0.16244	O31	0.06053	0.19114	0.15234
Si17	0.03387	0.26103	0.03387	O32	0.03388	0.22485	0.17241
Si18	0.03387	0.46613	0.13506	O33	0.00000	0.20945	0.14223
Si19	0.03387	0.41142	0.09511	O34	0.09699	0.14525	0.17950
Si20	0.03387	0.38246	0.03387	O35	0.13462	0.10243	0.18470
Si21	0.03387	0.06392	0.32175	O36	0.00000	0.24024	0.20258
Si22	0.05884	0.38630	0.15285	O37	0.13168	0.27599	0.19430
Si23	0.05800	0.44080	0.19308	O38	0.03387	0.39694	0.06449
O1	0.03387	0.38711	0.23030	O39	0.03387	0.38246	0.00000
O2	0.04654	0.42813	0.27874	O40	0.00000	0.38246	0.03387
O3	0.00000	0.41426	0.25055	O41	0.04890	0.35211	0.03387
O4	0.04594	0.42753	0.22182	O42	0.00000	0.06392	0.32175
O5	0.00000	0.35996	0.21005	O43	0.03387	0.04890	0.29139
O6	0.04954	0.33013	0.20664	O44	0.05842	0.41355	0.17297
O7	0.04636	0.37313	0.18145	O45	0.04636	0.39886	0.12398
O8	0.09159	0.28124	0.21263	O46	0.04594	0.45347	0.16407
O9	0.04954	0.27027	0.20290	O47	0.03387	0.26103	0.00000
O10	0.07890	0.31404	0.17546	O48	0.00000	0.26103	0.03387
O11	0.18354	0.17464	0.28768	O49	0.03387	0.43878	0.11509
O12	0.22185	0.22187	0.30475	O50	0.00000	0.46613	0.13506
O13	0.22865	0.18998	0.27286	O51	0.03387	0.50000	0.13506
O14	0.18829	0.23201	0.27119	O52	0.00000	0.41142	0.09511
O15	0.09663	0.17507	0.24033				

Table 4. Atomic coordinates for the **sod-t** framework, optimized as a silicate by GULP in cubic space group $Im\overline{3}m$, with $a = 28.822$ Å.

Atom	x	y	z
Si1	0.05185	0.12720	0.44905
Si2	0.05498	0.25724	0.33097
Si3	0.10658	0.18106	0.37978
O1	0.06258	0.16207	0.40749
O2	0.08189	0.08189	0.44297
O3	0.06037	0.15022	0.50000
O4	0.00000	0.11001	0.44358
O5	0.08002	0.29062	0.36736
O6	0.00000	0.25136	0.34252
O7	0.06040	0.27914	0.27914
O8	0.08463	0.20941	0.33619
O9	0.14120	0.14120	0.35987

Table 5. Atomic coordinates for the **fax** framework, optimized by GULP as a silicate in hexagonal space group $P6/mmm$, with $a = 32.585$Å and $c = 33.764$ Å.

Atom	x	y	z
Si1	0.37543	0.05463	0.27343
Si2	0.53138	0.15650	0.10571
Si3	0.35200	0.12958	0.45645
Si4	0.41614	0.05540	0.45693
Si5	0.57225	0.23863	0.04603
Si6	0.48025	0.05606	0.14182
Si7	0.27403	0.08923	0.39607
Si8	0.31595	0.05440	0.33816
Si9	0.49400	0.20034	0.16867
Si10	0.48368	0.05554	0.40040
Si11	0.44940	0.10462	0.20799
Si12	0.57561	0.24286	0.23142
Si13	0.19360	0.05163	0.45650
Si14	0.39854	0.11076	0.39684
Si15	0.45722	0.10178	0.33695
Si16	0.52824	0.14861	0.27258
O1	0.22538	0.05705	0.41866
O2	0.33938	0.16969	0.46475
O3	0.47547	0.23774	0.15865
O4	0.44689	0.12957	0.37217
O5	0.51141	0.18360	0.13137
O6	0.49497	0.09809	0.10761
O7	0.52946	0.05892	0.15610
O8	0.44380	0.00000	0.12835
O9	0.41353	0.07060	0.30829
O10	0.39961	0.08109	0.23218
O11	0.45975	0.00000	0.40520
O12	0.55494	0.20467	0.26626
O13	0.46933	0.06497	0.35734
O14	0.30020	0.00000	0.34789

Atom	x	y	z
O15	0.35519	0.00000	0.26397
O16	0.54024	0.08049	0.40282
O17	0.55979	0.23122	0.00000
O18	0.45423	0.06935	0.17658
O19	0.27480	0.06531	0.35340
O20	0.46769	0.07625	0.43676
O21	0.62421	0.24842	0.21454
O22	0.56459	0.12918	0.27548
O23	0.42274	0.07945	0.50000
O24	0.39907	0.14927	0.42801
O25	0.50147	0.14176	0.31360
O26	0.62743	0.25485	0.05373
O27	0.45281	0.15192	0.18878
O28	0.31155	0.08990	0.42825
O29	0.28326	0.14163	0.38687
O30	0.53887	0.18535	0.06454
O31	0.58258	0.16517	0.12054
O32	0.49305	0.11942	0.23728
O33	0.53935	0.22728	0.19587
O34	0.14836	0.00000	0.45491
O35	0.17301	0.08651	0.45211
O36	0.35627	0.11014	0.50000
O37	0.39103	0.00000	0.46192
O38	0.56380	0.28190	0.06172
O39	0.58492	0.29246	0.24939
O40	0.38531	0.06715	0.42700
O41	0.33321	0.06345	0.29145
O42	0.35929	0.09273	0.36333
O43	0.21980	0.06006	0.50000

Table 6. Atomic coordinates for the **fay** framework, optimized as a silicate by GULP in tetragonal space group $Fd\overline{3}m$, with $a = 23.575$ Å and $c = 40.327$ Å.

Atom	x	y	z	Atom	x	y	z
Si1	0.41016	0.50367	0.41559	O13	0.97307	0.27660	0.12405
Si2	0.34964	0.43862	0.46418	O14	0.01224	0.34857	0.22377
Si3	0.05090	0.13673	0.14536	O15	0.11787	0.34470	0.21227
Si4	0.01038	0.24985	0.15321	O16	0.04767	0.40156	0.16996
Si5	0.05717	0.34812	0.19394	O17	0.10741	0.37235	0.27874
Si6	0.14468	0.37277	0.24508	O18	0.20276	0.34187	0.25404
Si7	0.24681	0.33394	0.28370	O19	0.15651	0.43626	0.23349
Si8	0.41139	0.50227	0.28885	O20	0.21931	0.32548	0.32040
Si9	0.29768	0.45131	0.28412	O21	0.27627	0.27627	0.27305
Si10	0.98991	0.30915	0.25371	O22	0.29308	0.38360	0.28488
Si11	0.07770	0.33029	0.30521	O23	0.45356	0.45356	0.30196
Si12	0.18109	0.27764	0.33859	O24	0.44988	0.55012	0.26911
Si13	0.19426	0.29140	0.46095	O25	0.35918	0.47175	0.26988
Si14	0.12864	0.33737	0.40090	O26	0.25316	0.47699	0.25893
Si15	0.03272	0.40087	0.36706	O27	0.03044	0.29702	0.28462
Si16	0.02912	0.42284	0.13356	O28	0.12069	0.28094	0.31862
Si17	0.17133	0.46494	0.40107	O29	0.04605	0.36922	0.33248
Si18	0.21982	0.41846	0.46413	O30	0.21621	0.21621	0.33908
O1	0.35798	0.49084	0.43940	O31	0.16259	0.29712	0.37518
O2	0.45676	0.45676	0.42175	O32	0.23875	0.23875	0.45223
O3	0.43491	0.56509	0.42508	O33	0.17537	0.28445	0.50000
O4	0.39073	0.50239	0.37764	O34	0.22309	0.35192	0.45434
O5	0.38041	0.38041	0.45197	O35	0.13934	0.30152	0.43561
O6	0.37445	0.45545	0.50000	O36	0.15262	0.40032	0.39569
O7	0.28401	0.43294	0.46676	O37	0.06163	0.35562	0.39379
O8	0.03540	0.11930	0.18212	O38	0.96662	0.41883	0.37612
O9	0.11304	0.11304	0.13637	O39	0.05550	0.46476	0.36364
O10	0.05349	0.20358	0.13848	O40	0.01727	0.37313	0.10587
O11	0.96925	0.21653	0.17830	O41	0.18974	0.46344	0.43956
O12	0.05120	0.29310	0.17158	O42	0.18944	0.42569	0.50000

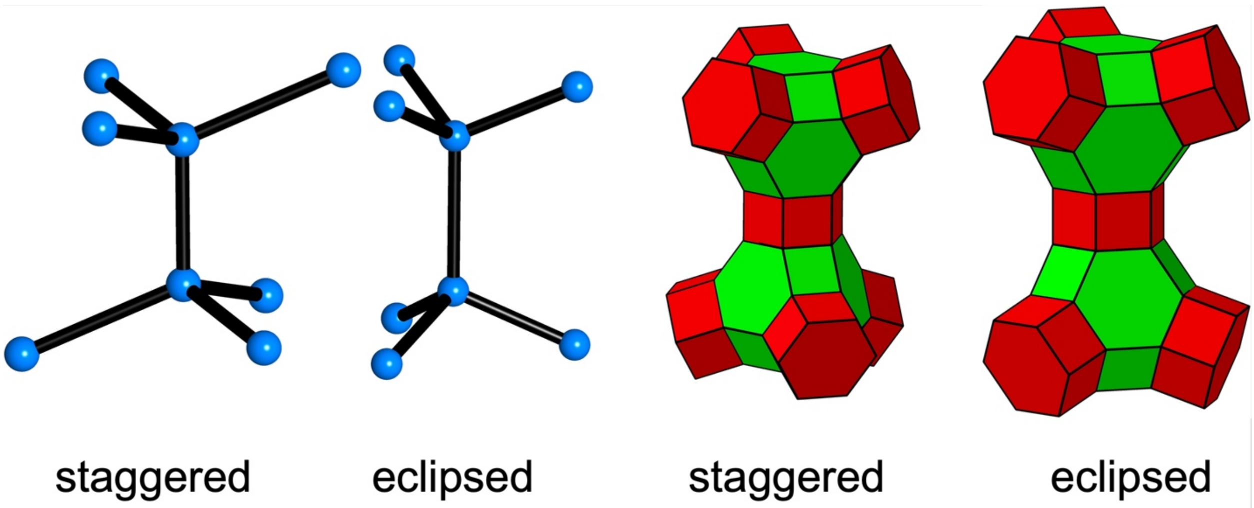

Figure 1. (Left) Illustration of the staggered and eclipsed configurations in tetrahedral nets, and (right) in expanded form as two joined SP_4 tetrahedral units (S ≡ sodalite cage, P ≡ hexagonal prism). The tetrahedral nets of the staggered and eclipsed configurations of the SP_4 forms experience no torsional strain about the S–P–S axes. The P–S–P angle is the tetrahedral angle, 109.47°, and the S–P–S angle is 180°.

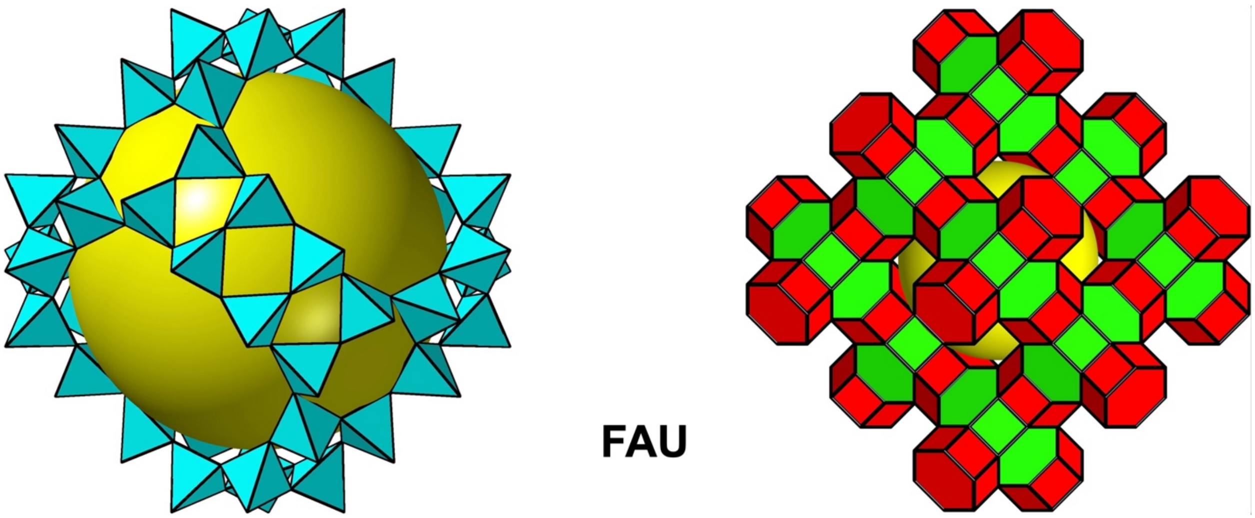

Figure 2. The **FAU** cage formed by linked SiO_4 tetrahedra (left) and by the augmented cristobalite **-t** net represented as SP_4 tetrahedral units (right). The maximum included sphere is represented by the yellow ball.

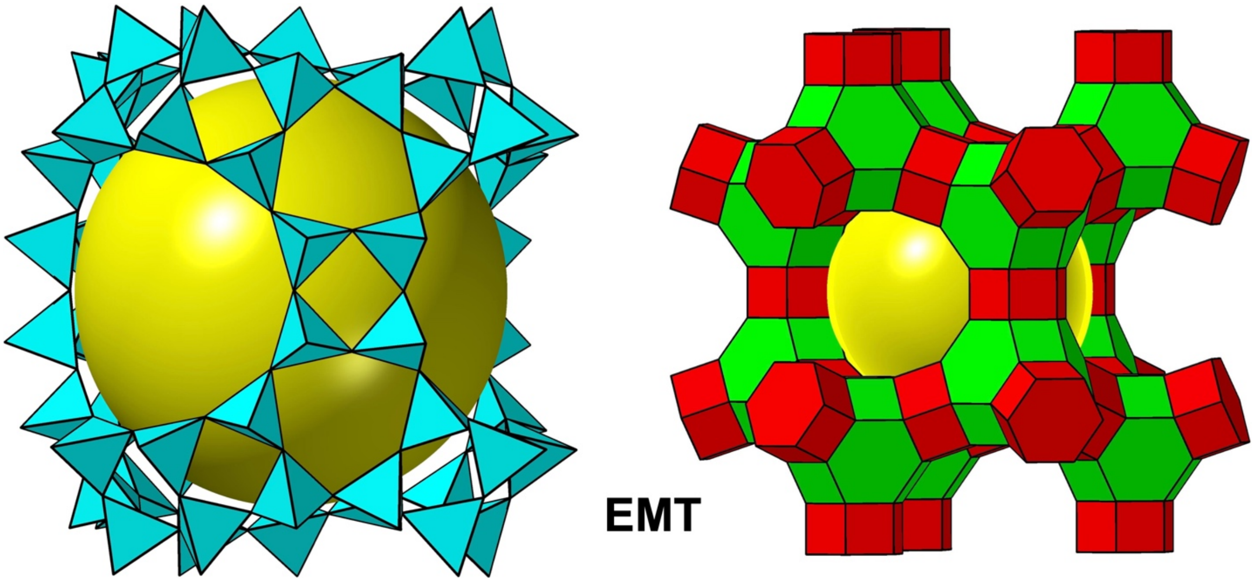

Figure 3. The **EMT** cage formed by linked SiO_4 tetrahedra (left) and by the augmented lonsdaleite **-t** net, represented as SP_4 tetrahedral units (right). The maximum included sphere is represented by the yellow ball.

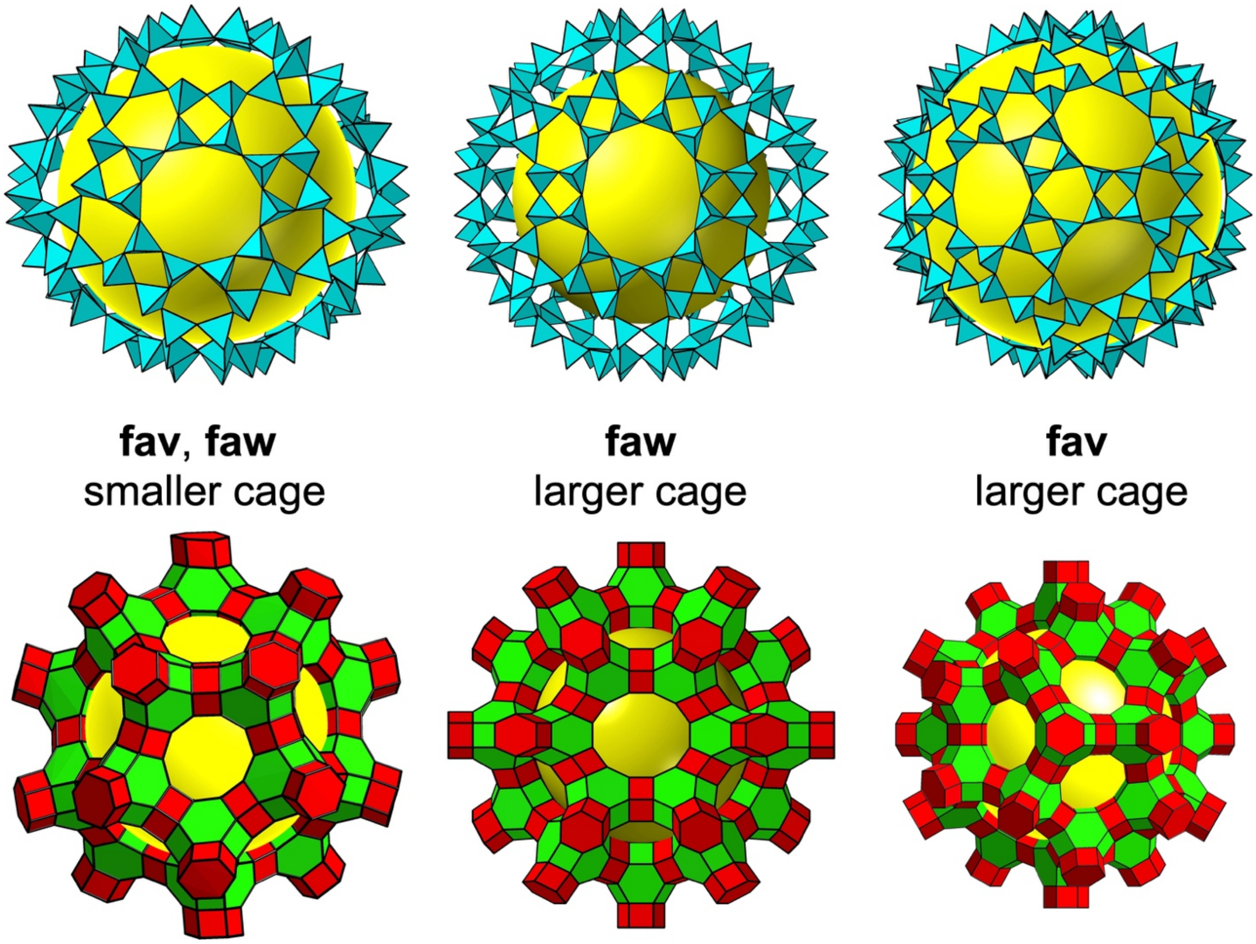

Figure 4. The cages in **fav** and **faw** delineated by linked SiO_4 tetrahedra (top) and depicted as linked SP_4 tetrahedral units (bottom). The maximum included sphere is represented by the yellow ball.

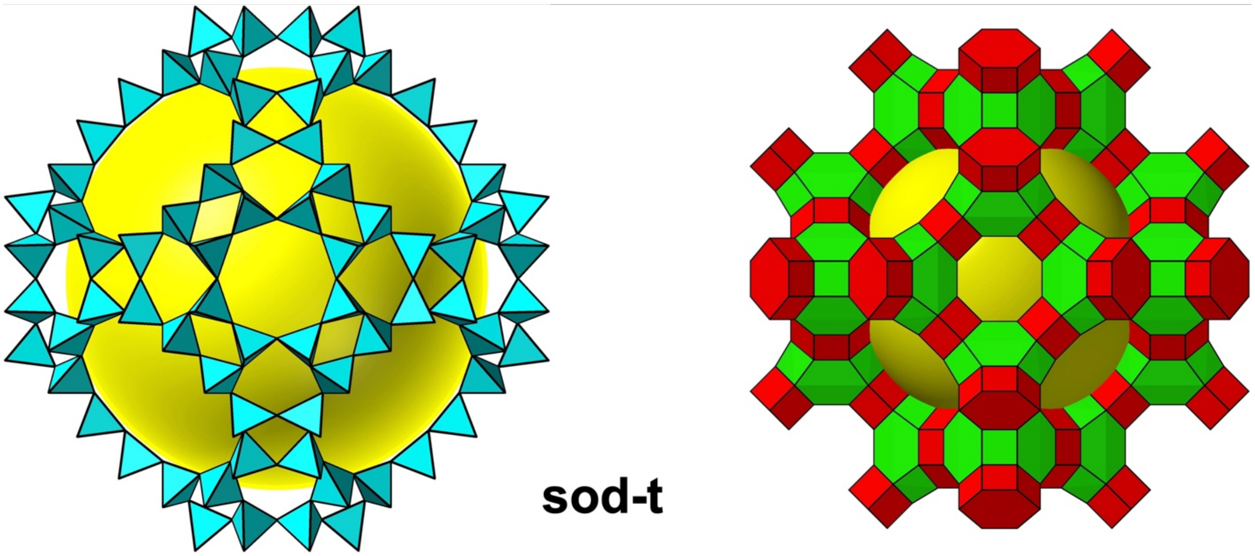

Figure 5. The cage in **sod-t** formed outlined by linked SiO_4 tetrahedra (left) and shown as linked SP_4 tetrahedral units (right). The maximum included sphere is represented by the yellow ball.

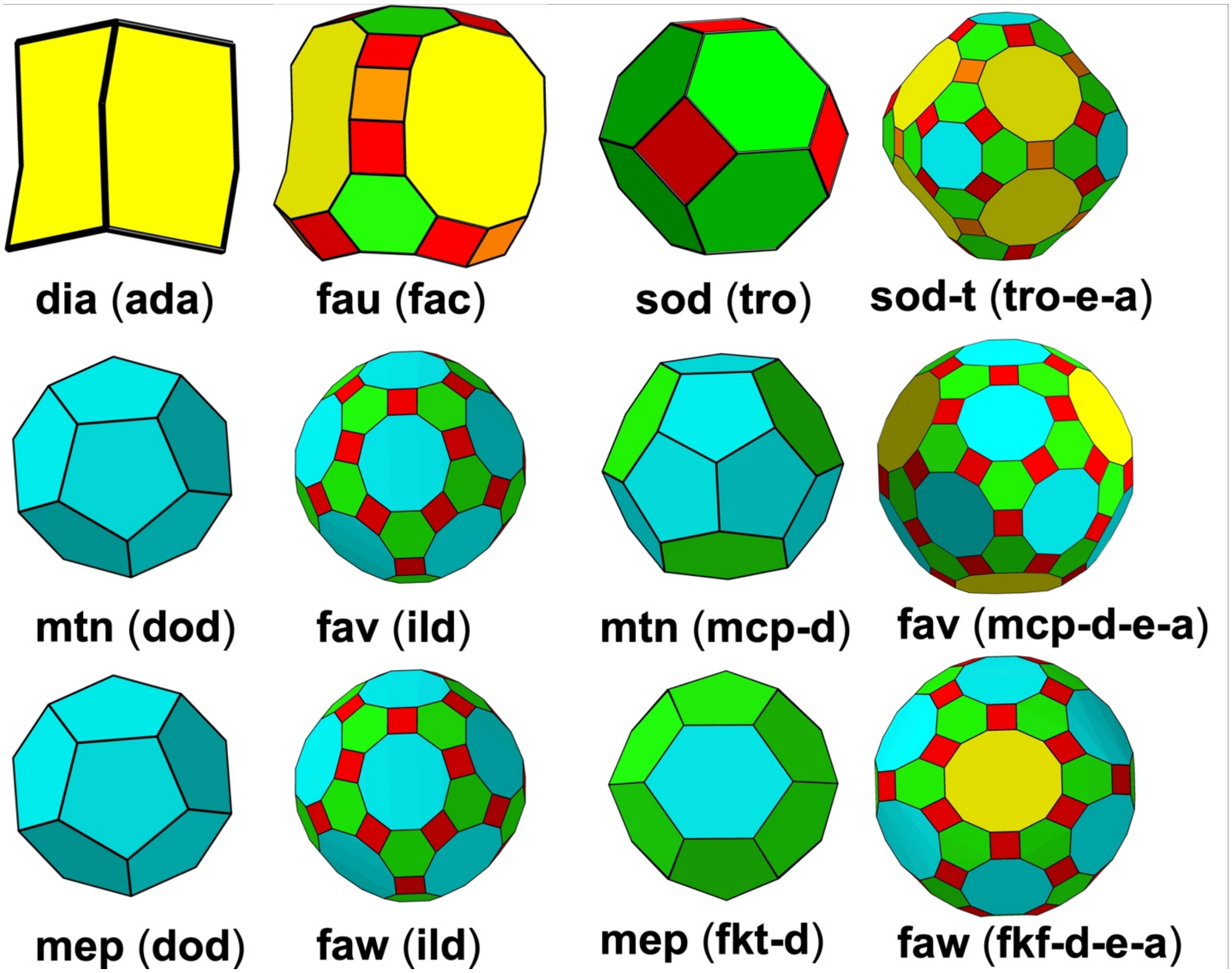

Figure 6. Illustration of the polyhedral units defining cages in various nets. Symbols in parentheses are RCSR symbols for individual polyhedra.

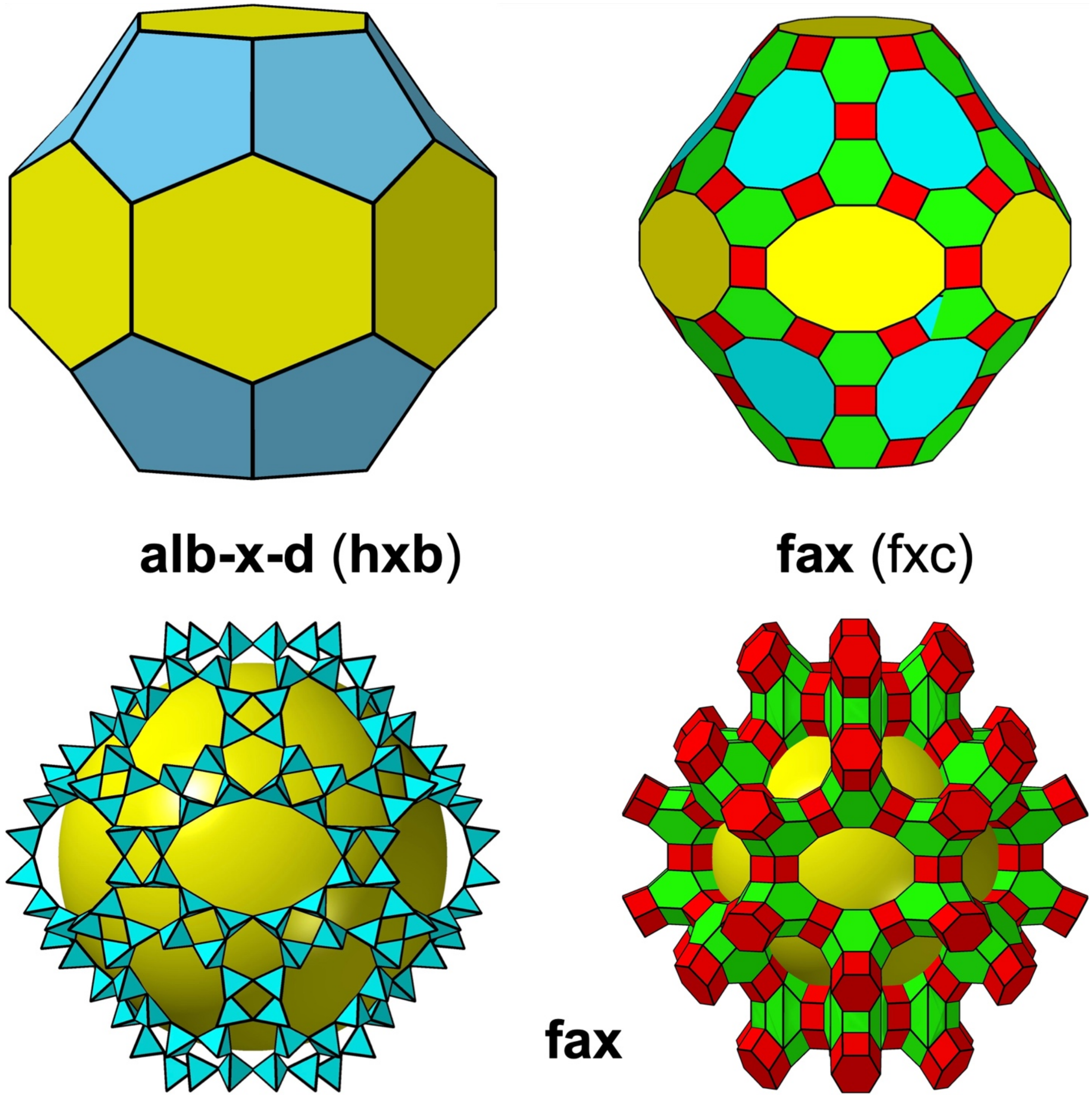

Figure 7. Top row: The polyhedral units (symbols in parentheses) defining cages in **alb-x-d** and for the augmented **fax** framework. Bottom row: The cage in **fax** shown as linked SiO_4 tetrahedra (left) and shown as linked SP_4 tetrahedral units (right). The maximum included sphere is represented by the yellow ball. Distortion of the SP_4 units is visible.

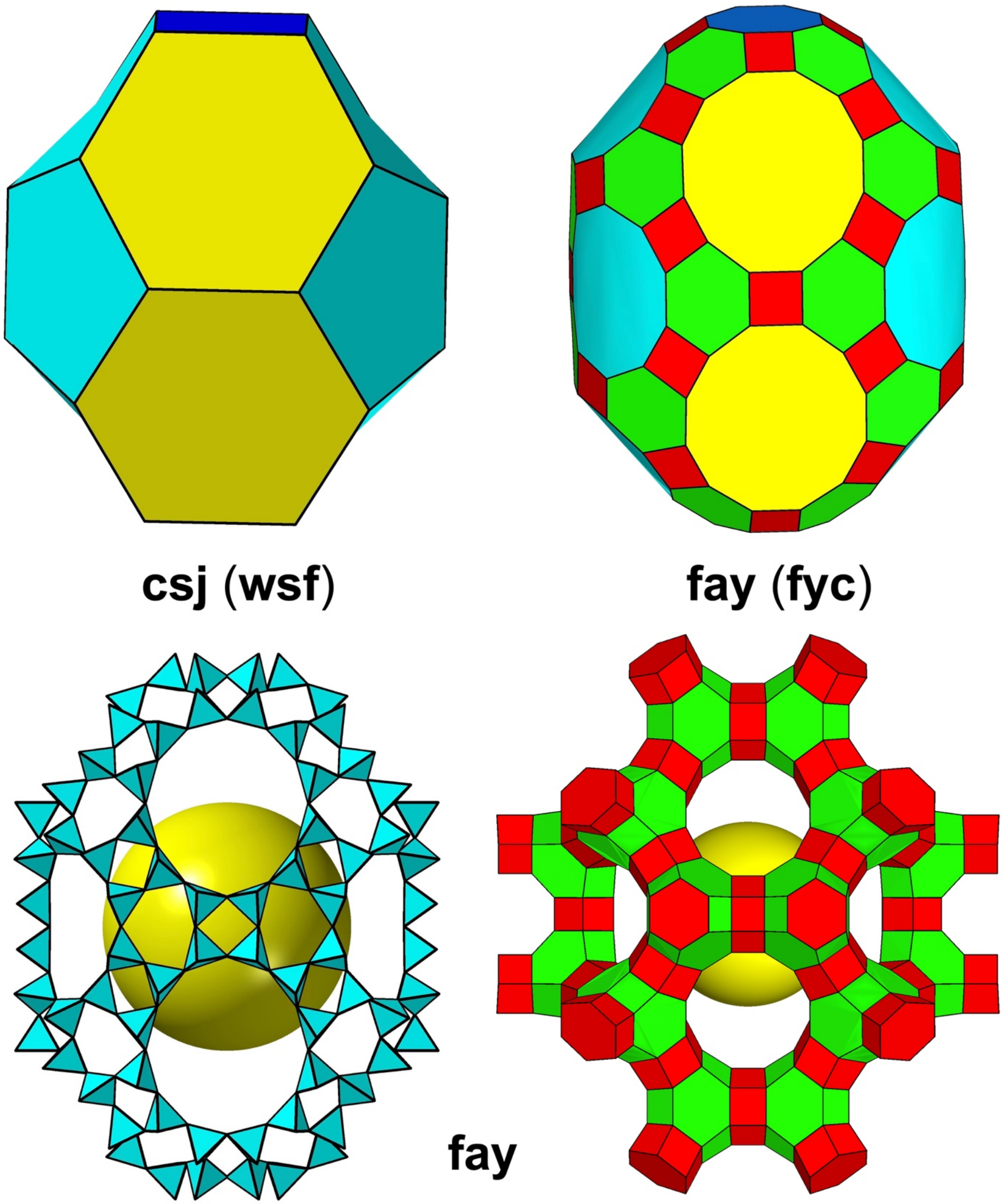

Figure 8. Top row: The polyhedral units (symbols in parentheses) defining cages in **csj** and for the augmented **fay** framework. Bottom row: The ellipsoidal cage in **fay** shown as linked SiO_4 tetrahedra (left) and as linked SP_4 tetrahedral units (right). The maximum included sphere is represented by the yellow ball: the sphere diameter is limited by the ellipsoidal cage. Strong distortion of some of the SP_4 units is visible.