Enumeration of periodic tetrahedral frameworks. II. Polynodal graphs

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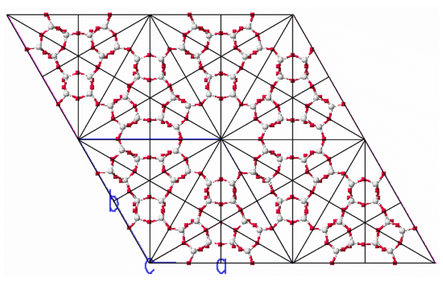
Introduction:

Zeolite frameworks can be described as periodic 4-connected graphs. Previously, we described a method for enumerating both uninodal and polynodal periodic 4-connected graphs [1,2]. The method finds graphs by performing a symmetry-constrained combinatorial search over all possible permutations of bonds between atoms sitting in all possible combinations of crystallographic sites for each space group. At that time, the combinatorial explosion of graphs discovered, as a function of unique atoms, was overwhelming, and we restricted our attention to the uninodal graphs and the 48 binodal graphs of space group *P*6/*mmm*. We have since improved both the efficiency of the combinatorial algorithm, and the sophistication of the framework annealer. In addition, a 32-processor Beowulf cluster is now dedicated to the problem, allowing us to focus our attention on the plausible (low framework energy) regular tetrahedral polynodal nets. We have applied the method to enumerate all possible solutions to the elusive ZSM-10 framework in space group P6/mmm with 6 unique T-atoms, producing some beautiful and highly plausible candidate frameworks. One of these produces a diffraction pattern in good agreement with that from ZSM-10. The others make attractive synthetic targets.

The combinatorial search is described diagrammatically below.

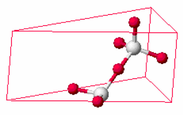
The LTL framework has *P*6/*mmm* symmetry



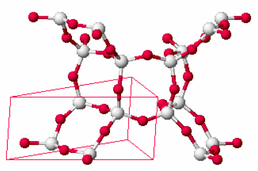
All of the symmetry operations can be generated by mirrors

LTL Framework

LTL fundamental region contains 2 T-atoms and 6 unique Oxygen atoms, and is bounded by 5 mirror planes.

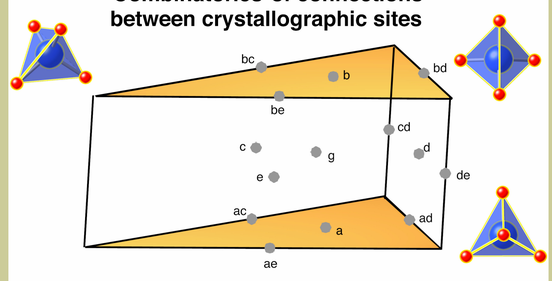


Each T-atom is connected to four oxygens



The LTL framework is generated by the action of the mirror planes, much in the same way as a kaleidascope works.

Combinatorics of connections between crystallographic sites



There are 14 connectable sites for tetrahedra in the P6/mmm fundamental region. The rules for interconnections depend on the site.

A set of simple rules helps limit the number of combinatorial possibilities

(1) No T-atom can lie on a 6-fold axis

(2) No T-atom, or T-atom vertex, can lie on a vertex of the fundamental region

(3) If a T-atom lies on a face of the fundamental region, then two (and only two) of the T-atom vertices lie on that same face. (otherwise it is planar))

(4) Connections to atoms outside the fundamental region must involve either a T-atom, or one of its vertices, that lies on a mirror (or on an edge defined by two perpendicular mirrors).

(5) All T-atoms are connected to four other T-atoms.

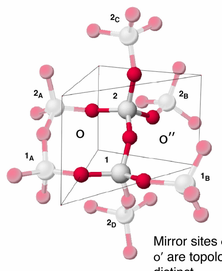
(6) Tetrahedra are denied edge- and face-sharing connectivities.

(7) Each of the five faces of the fundamental region must have at least one bond connecting through it. (For 3-dimensional connectivity)

Directed Graph Description – LTL

Atom site list

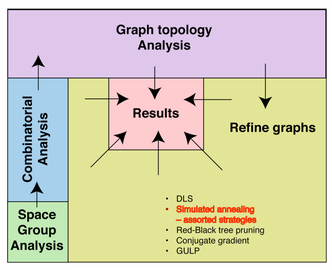
Atom id	operator	Atom id	
1	(*x*, *x*–*y*, *z*)	1	— (1_A)
1	(*x*–*y*, –*y*, *z*)	1	— (1_B)
1	(*x*, *y*, *z*)	2	— (2)
2	(*x*, *y*, *z*)	1	— (1)
1	(*x*, *y*, –*z*)	2	— (2_D)
2	(*x*, *x*–*y*, *z*)	2	— (2_A)
2	(1–*x*+*y*, *y*, *z*)	2	— (2_B)
2	(*x*, *y*, 1–*z*)	2	— (2_C)

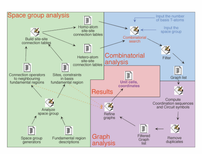


Mirror sites o and o′ are topologically distinct.

Oxygen atoms are implied by the Si–Si bonds, and are therefore redundant.

Surprisingly, most of the effort is in refining the graphs





The effort planned assumed that the refining would be quick and easy

Imbedding the graphs in real space – refining them – has been arduous, and is an ongoing struggle. Speed and efficiency are low.

Spacegroup	T-atoms	Graphs	
225	1	3	
225	2	13	
225	3	135	
225	4	1,746	
225	5	23,841	
225	6	355,029	
225	7	5,709,628	
191	1	0	
191	2	48	
191	3	1,337	
191	4	31,230	
191	5	743,423	
191	6*	579,270	(*subset of sites)
191	6	18,400,408	
87	1	5	
87	2	3,075	
87	3	2,665,596	
87	4*	176,882,198	(* did not finish)
230	1	71	
230	2	88,085	
230	3	121,925,278	
227	1	6	
227	2	108	
227	3	3,152	
227	4	113,511	
227	5	4,787,424	

- The table shows the number of graphs enumerated for several space groups.
- For a selection of high symmetry space groups such as 225, 191 or 227, refinement of graphs up to n=7, 6 & 5 respectively is possible. For most space groups n=3 or 4 is our limit with current resources, e.g. the table shows the explosion in numbers of enumerated graphs for space groups 87 and 230.
- The graph descriptor for LTL is shown. Together with look-up tables of the operators for space group 191 this graph identifies the LTL topology.

LTL graph

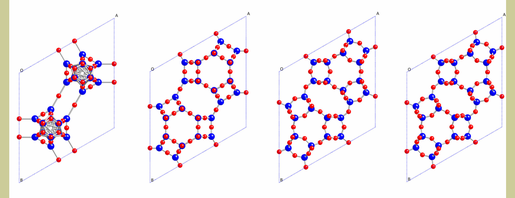
191
2
0 15
6
0 33 0
0 46 0
0 47 0
0 0 1
1 12 1
1 24 1

Methods:

- Refinement of graphs into atomistic models of Si and O atoms is computationally expensive. However, with the aid of a 32 processor cluster we have refined ~579,000 graphs in three weeks.
- The first stages of the refinement places each atom at the geometric center of its bonded neighbors. Oxygen atoms are held mid-way between Si atoms as only T atoms are annealed based on a cost-function of T-T bond distances and angles fitted to quartz.
- If the initial refinement is successful, T and O atoms are annealed while insuring the topology remains as defined by its graph. An implementation of the BGB cost-function[3] is used. To optimize the annealing process, several parallel anneals are conducted with a generic algorithm. GULP[4] is used for further refinement of favorable structures.

Stages of refinement

Example, LTL, space group P6/mmm (191) two unique T-atoms



Place atoms at the geometric center of their neighbours. Refine unit cell only using "regular tetrahedral" forces on T-atoms

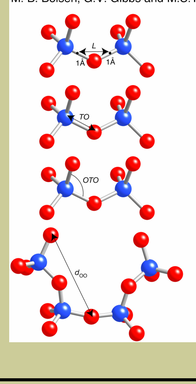
RefineT-atoms and unit cell parameters using "regular tetrahedral" forces on T-atoms

RefineT-atoms, O-atoms and unit cell parameters Using Boisen-Gibbs-Bukowinski force model

RefineT-atoms, O-atoms and unit cell using GULP (J. Gale)

Boisen-Gibbs-Bukowinski force model

M. B. Boisen, G.V. Gibbs and M.S.T. Bukowinski, Phys. Chem. Minerals (1994) **21** 269 – 284



$$U_{BGB} = A\sum_{O}(L-L_0)^2 + B\sum_{T}(OTO-OTO_0)^2 + C\sum_{T}(TO-TO_0)^2 + D\sum_{T}\sum_{O}(L-L_0)(TO-TO_0) + E\sum_{d_{OO}>4Å}\exp(-F\,d_{OO}+G)$$

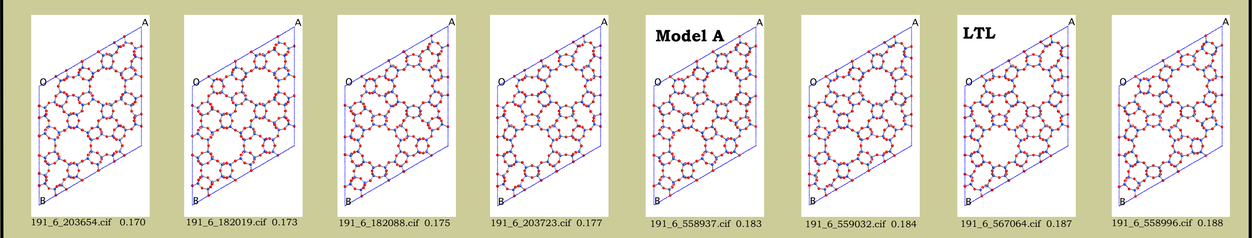
Empirical force field derived from ab-initio modelling of Si_2O_7, and fitting to quartz compressibility data.

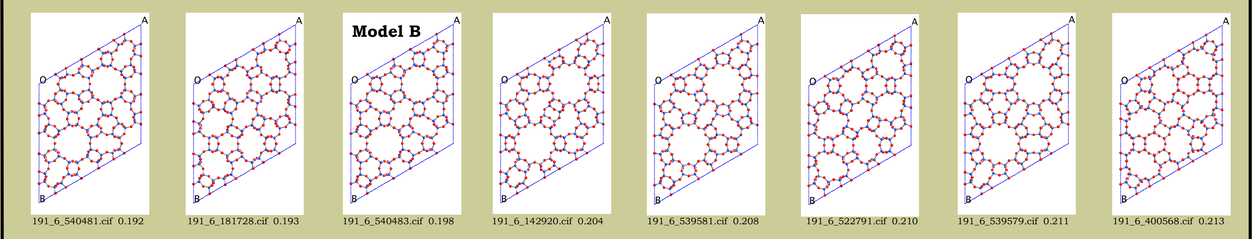
Most terms relate to the local T_2O_7 cluster.

The non-codimer repulsion terms (d_{OO}) are computationally expensive.

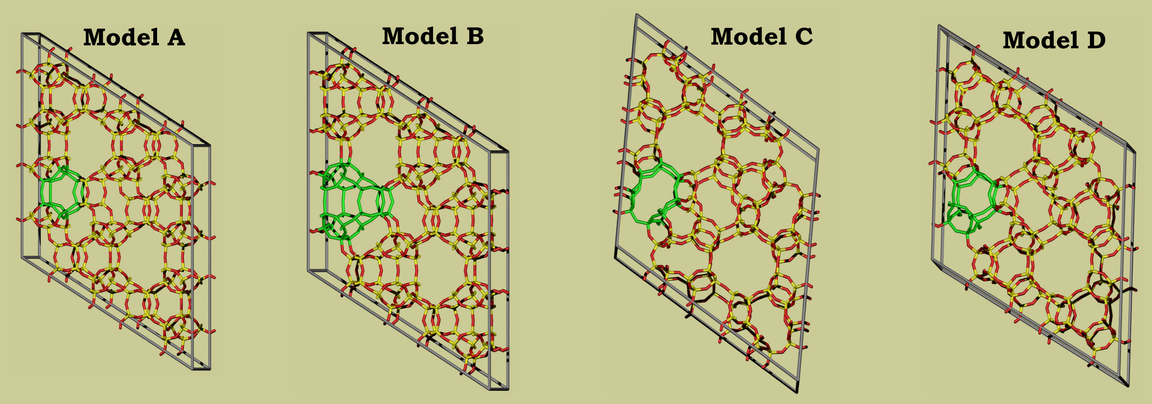
Application: Structure determination of ZSM-10

- In a paper "ZSM-10: Synthesis and tetrahedral framework structure" (Higgins and Schmitt[5]), two models are proposed for ZSM10, Models A & B (also shown below).
- From our enumeration method we can systematically eliminate all possible solutions for space group 191 with n=6 T atoms. Approximately 70 structures of 579,270 graphs (a subset of 191 n=6) with favorable GULP energies and suitable lattice parameters remain. Below are the 16 best structures including models A & B and LTL in order of energy relative to quartz (in eV per SiO_2).





- Comparison with simulated XRD patterns further reduces the number of likely candidates.
- Two more models (in addition to A & B) stand out, 191_6_203654 (Model C) & 191_6_182091 (Model D). Views of these structures are given below.
- Initial results confirm that Model A is still the best candidates for ZSM-10.



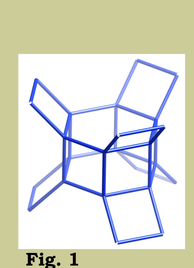


Fig. 1

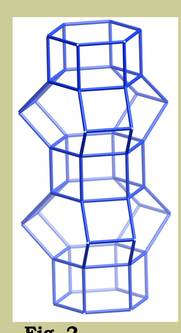


Fig. 2

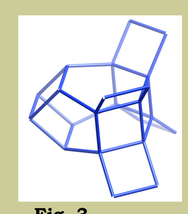


Fig. 3

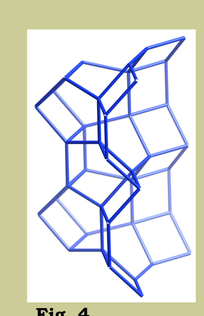
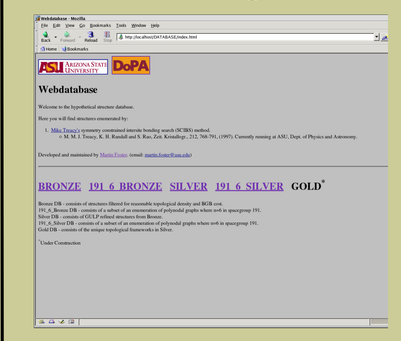


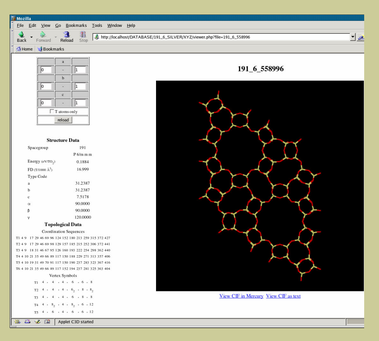
Fig. 4

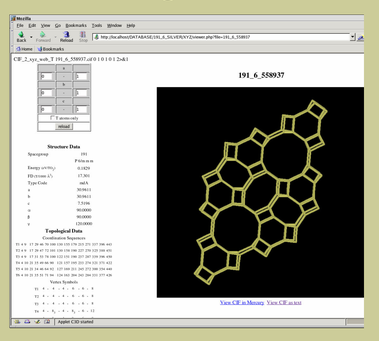
Diagrams of T atom connectivity in Fig. 1 & Fig. 2 show double six rings and stacking for LTL, Models A & B. In Fig. 3 & Fig.4 the diagrams show 5 member-rings present in Models C & D.

Database of enumerated structures on the web

Processed graphs are archived in the CIF file format and entered in a searchable database. The database is structured into sections (bronze, silver and gold), indicating the level of refinement of the graphs. A website acts as an interface between our the MySQL database and the CIF file collection enabling users to view and download structures. Below are some images of the website.







Conclusions

Our enumeration and refinement method can be successfully applied to polynodal graphs, e.g. space group 191 n=6. An application in the structure determination for ZSM-10 has been demonstrated. We have refined all enumerated graphs for a subset of space group 191 with 6 unique T atoms which corresponds to all possible structure solutions for ZSM-10. So far, by process of elimination, the originally proposed structure (Model A) remains the best fit to experimental data.

A website acting as an interface between our database and structure files is now available under
http://www.public.asu.edu/~mtreacy/

Acknowledgments:

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