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# Computational analysis of mineral structures

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# Some naturally occurring zeolites

*most synthetic zeolites are polycrystalline*

Chabazite



Ferrerite



Natrolite



Phillipsite



# Zeolite, what is it?

## ➤ Origin

- boiling stone; from Greek: zein--"to boil"; lithos--"a stone" (1756, Swedish scientist A. F. Cronstedt)

## ➤ Definition

- **A loose definition:** *“a zeolite is an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion-exchange and reversible dehydration”.* (J. V. Smith, Chem. Rev. 1988)
- **Definition after the International Mineralogical Association, Commission on New Minerals and Mineral Names:** *“A zeolite mineral is a crystalline substance with a structure characterized by a framework of linked tetrahedra, each consisting of four O atoms surrounding a cation. This framework contains open channels and cages. These are usually occupied by H<sub>2</sub>O molecules and extra-framework cations that are commonly exchangeable. The channels are large enough to allow the passage of guest species. In the hydrated phases, dehydration occurs at temperatures mostly below about 400°C and is largely reversible. The framework may be interrupted by (OH, F) groups; these occupy a tetrahedron apex that is not shared with adjacent tetrahedral”* (COOMBS et al. 1997, 1998)



# Major applications of zeolites

## ➤ Adsorbent

➤ Purification, drying, separation, etc.

## ➤ Ion exchange

➤ Water softening, waste treatment, fertilizers, etc.

## ➤ Heterogeneous Catalysis

➤ All kinds of organic and inorganic reactions.

➤ Most important: petrochemical industry.



<http://en.wikipedia.org/wiki/Image:Gas-pump-Indiana-USA.jpg>

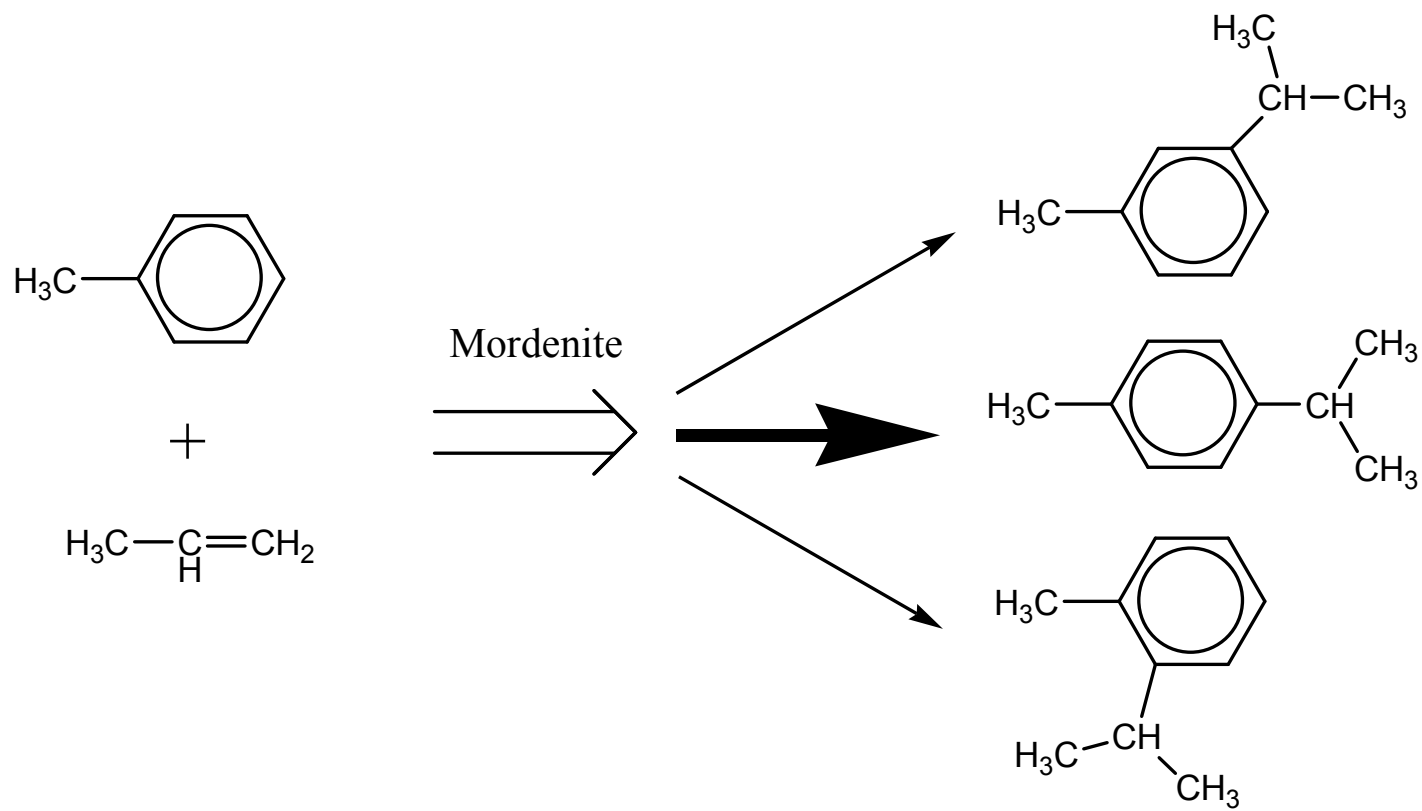
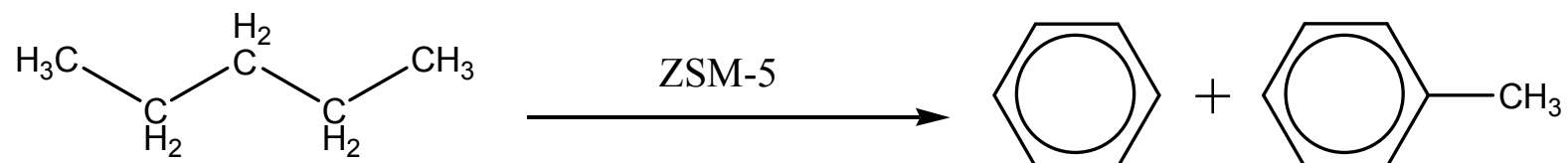
# High gasoline prices?

# Might be worse— Without zeolites!



[http://www.exxonmobil.com/NA-English/PA/about\\_where\\_ref\\_br.aspx](http://www.exxonmobil.com/NA-English/PA/about_where_ref_br.aspx)

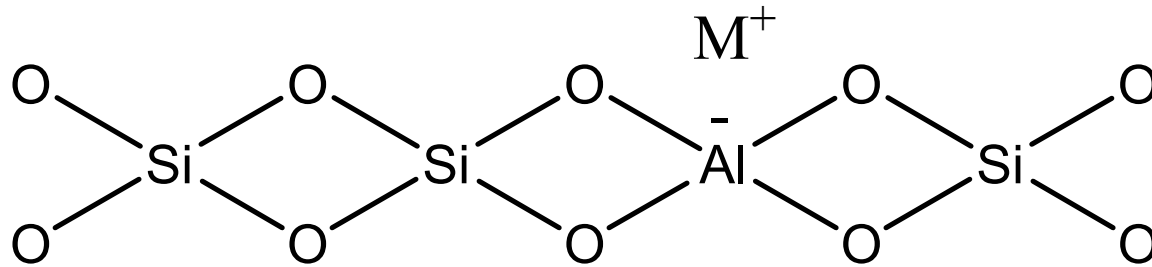
# Zeolite catalyzed petrochemical processes



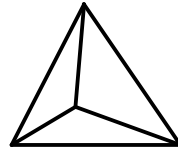
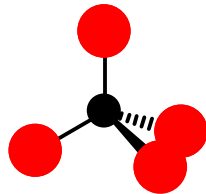
# General chemical formula of zeolites



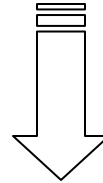
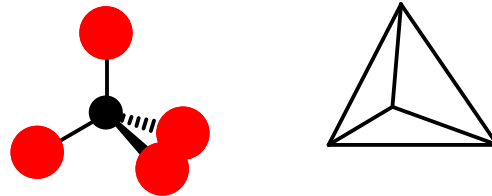
## Planar illustration of the structure



## Primary Building Units (PBU), $\text{TO}_4$

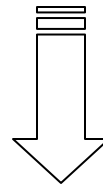


Primary Building Units (PBU)



Secondary Building Units (SBU)

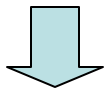
Composite Building Units (CBU)



Zeolite Frameworks

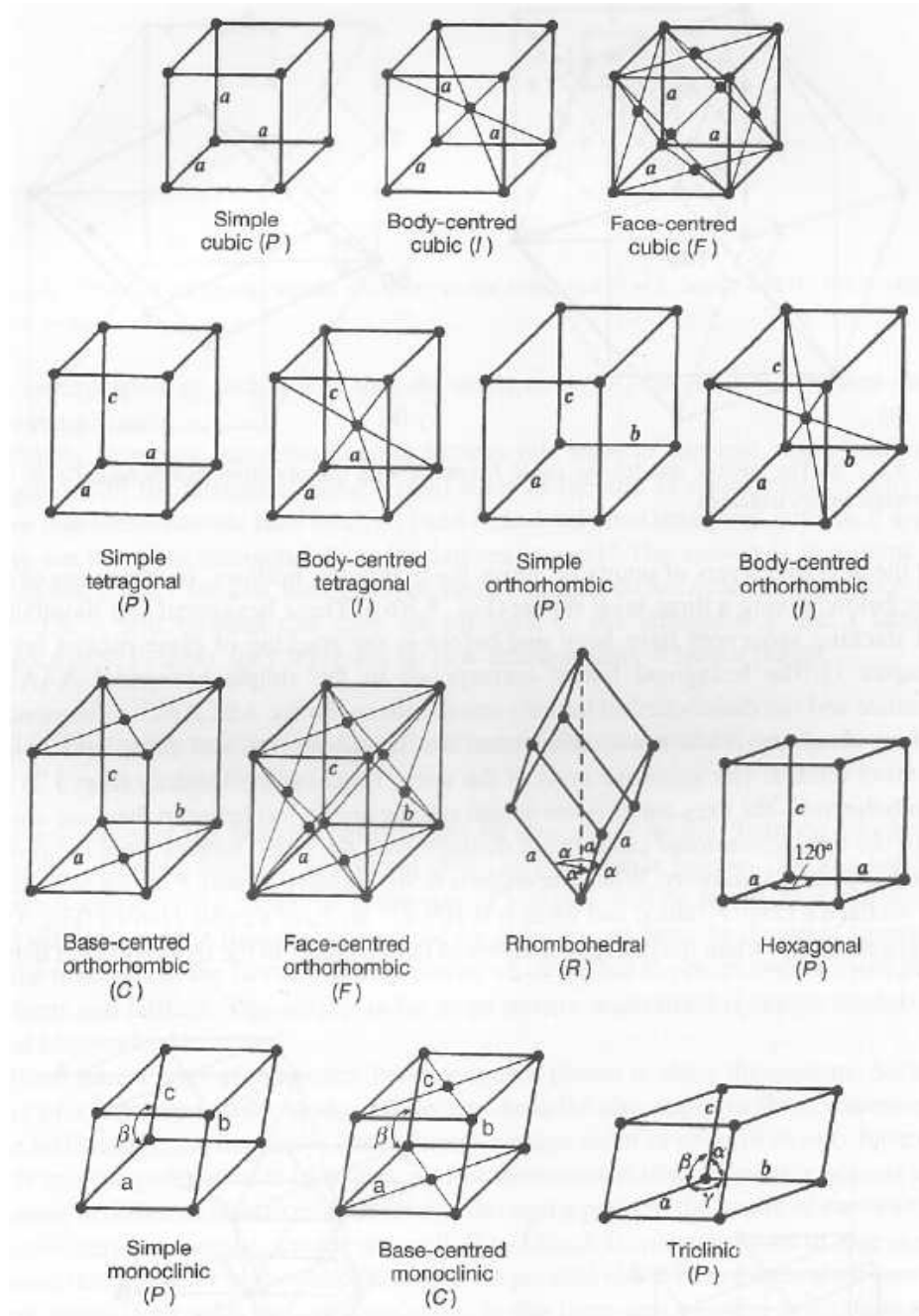
# •Seven Crystal Systems

- Triclinic
- Monoclinic
- Orthogonal
- Tetragonal
- Hexagonal
- Trigonal/Rhombohedral
- Cubic



The fourteen 3D lattices  
(*Bravais lattices*)

...unit cells in three dimensions



Prof. Travis Holman, CHEM-517, "X-ray Crystallography and Molecular Structure"

# 230 Space Group Diagrams and Tables

<http://img.chem.ucl.ac.uk/sgp/large/sgp.htm>

## Triclinic

1.  $\underline{P1}$       2.  $\underline{P-1}$

## Monoclinic

3.  $\underline{P121}$       4.  $\underline{P12_11}$       5.  $\underline{C121}$       6.  $\underline{P1m1}$       7.  $\underline{P1c1}$

## Orthorhombic

16.  $\underline{P222}$       17.  $\underline{P222_1}$       18.  $\underline{P2_12_12}$       19.  $\underline{P2_12_12_1}$       20.  $\underline{C222_1}$

## Tetragonal

75.  $\underline{P4}$       76.  $\underline{P4_1}$       77.  $\underline{P4_2}$       78.  $\underline{P4_3}$       79.  $\underline{I4}$

## Trigonal

143.  $\underline{P3}$       144.  $\underline{P3_1}$       145.  $\underline{P3_2}$       146.  $\underline{R3}$       147.  $\underline{P-3}$

## Hexagonal

168.  $\underline{P6}$       169.  $\underline{P6_1}$       170.  $\underline{P6_5}$       171.  $\underline{P6_2}$       172.  $\underline{P6_4}$

## Cubic

195.  $\underline{P23}$       196.  $\underline{F23}$       197.  $\underline{I23}$       198.  $\underline{P2_13}$       199.  $\underline{I2_13}$

# Framework types of zeolites

- **Classification of zeolites by framework types**
  - Meier and Olson, 1970
  - A framework type simply describes the connectivity of the tetrahedrally connected T atoms in the highest possible symmetry.
  - Without reference to the existence of cations, adsorbed phase, framework composition, observed symmetry, and the actual unit cell dimensions.
  - More fundamental than using “structures”
  
- **Framework type codes (FTC; previously called structure type codes)**
  - Following the rules set up by an IUPAC Commission on Zeolite Nomenclature in 1978(4), designations consisting of three capital Roman letters have been used throughout. The codes are generally derived from the names of the type materials. The assignment of Framework Type codes is subject to review and clearance by the IZA Structure Commission.

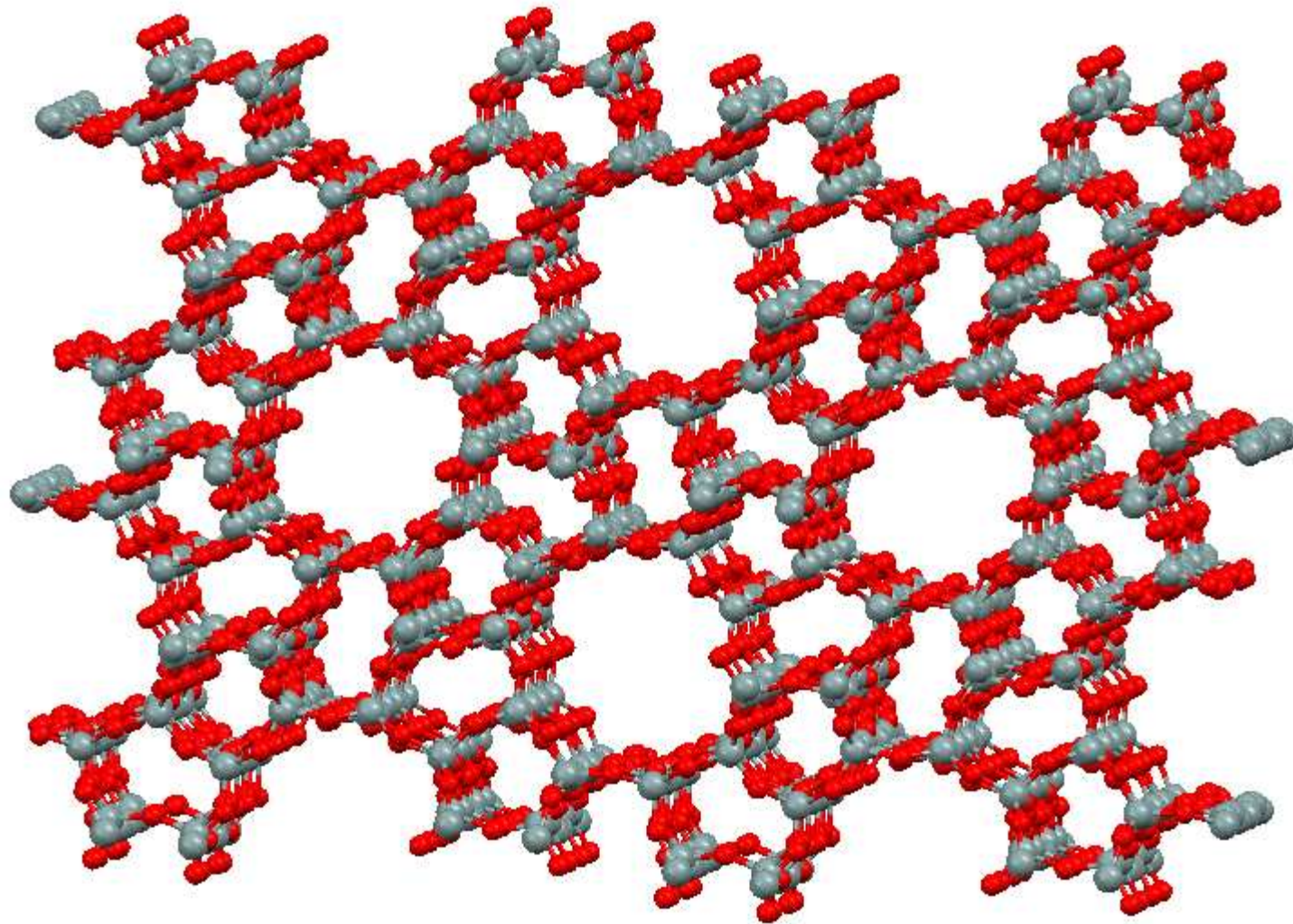
### Rules for Framework Type Assignment

The following is a set of rules to be applied by the Structure Commission of the IZA in assigning a three-letter code to a new framework type. The materials of interest are generally defined as open 4-connected 3D nets which have the general (approximate) composition  $AB_2$ , where A is a tetrahedrally connected atom and B is any 2-connected atom, which may or may not be shared, between two neighboring A atoms. Inclusion of other microporous materials is left to the discretion of the IZA Structure Commission, depending on the interest of the molecular sieve science community at large.

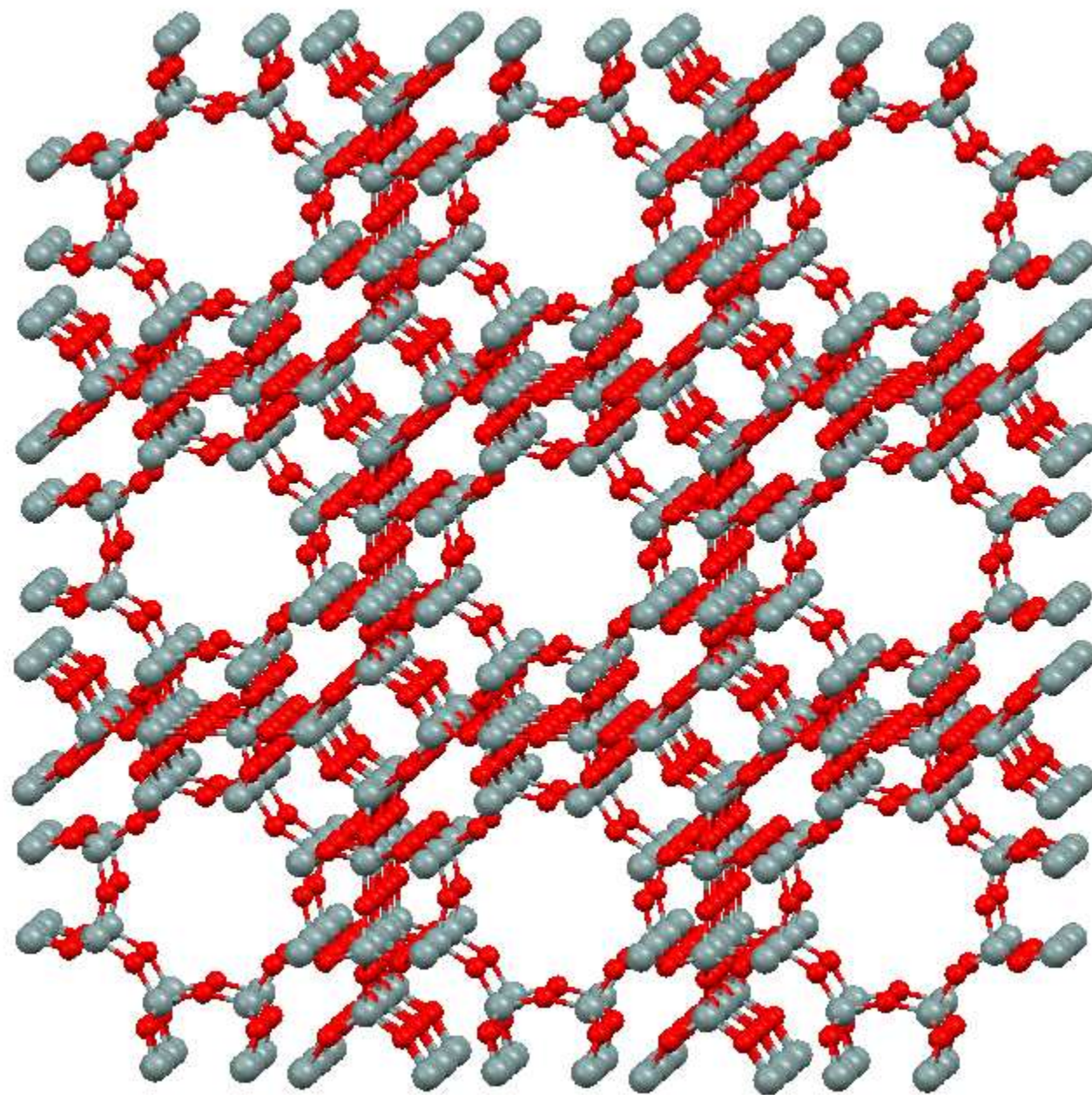
#### RULES

- (i) The IZA Structure Commission is the only body that can coordinate the assignment of a code to such frameworks. The framework types are idealized, with no reference to actual materials, symmetry, composition, etc. and, therefore, ONLY refer to the connectivity.
- (ii) The code for a 4-connected 3D framework type shall consist of three capital letters. Other frameworks of interest shall be indicated by a (-) in front of the code.
- (iii) The three letters of the code shall be mnemonic and must refer to an actual material (i.e. the type material). These materials are chosen to be:
  - mineral names (rules of the International Mineralogical Association followed).
  - commonly accepted synthetic material types.
  - in the absence of the above, the workers who first determined the structure have priority in assigning the name.
- (iv) No mnemonic code can be assigned without the structure being determined with the following exception:

For "polytypic" materials, codes can be assigned as useful. Such codes shall be marked with an asterisk.
- (v) Codes of framework types which turn out to be in error are discredited. Later use of the code is not permitted.
- (vi) For all cases where a decision of the Structure Commission is required, a two thirds majority vote of the full commission shall be required. Such votes are taken verbally at a meeting of the Structure Commission or are done in writing on the initiative of the Chairperson and Co-chairperson. All evidence substantiating a new framework type must accompany the ballot. The members are obliged to respond to this request within one month and the Chairperson and Co-chairperson will make all possible effort to solicit replies from all members.



MFI (orthorhombic system)



LTA (cubic system)

# Database of Zeolite Structures

IZA-SC

Framework Type

References

Powder Patterns

Building Schemes

Disordered Structures

Other Links

Advanced Search

Credits

Help

## Zeolite Framework Types

Enter the name of a zeolite material

Material name

Contains



find FTC

or select a Framework Type Code (FTC):

ABW	ACO	AEI	AEL	AEN	AET	AFG	AFI	AFN	AFO	AFR	AFS
AFT	AFX	AFY	AHT	ANA	APC	APD	AST	ASV	ATN	ATO	ATS
ATT	ATV	AWO	AWW	BCT	*BEA	BEC	BIK	BOG	BPH	BRE	CAN
CAS	CDO	CFI	CGF	CGS	CHA	-CHI	-CLO	CON	CZP	DAC	DDR
DFO	DFT	DOH	DON	EAB	EDI	EMT	EON	EPI	ERI	ESV	ETR
EUO	EZT	FAR	FAU	FER	FRA	GIS	GIU	GME	GON	GOO	HEU
IFR	IHW	IMF	ISV	ITE	ITH	ITW	IWR	IWV	IWW	JBW	KFI
LAU	LEV	LIO	-LIT	LOS	LOV	LTA	LTL	LTN	MAR	MAZ	MEI
MEL	MEP	MER	MFI	MFS	MON	MOR	MOZ	MSE	MSO	MTF	MTN
MTT	MTW	MWW	NAB	NAT	NES	NON	NPO	NSI	OBW	OFF	OSI
OSO	OWE	-PAR	PAU	PHI	PON	RHO	-RON	RRO	RSN	RTE	RTH
RUT	RWR	RWY	SAO	SAS	SAT	SAV	SBE	SBN	SBS	SBT	SFE
SFF	SFG	SFH	SFN	SFO	SGT	SIV	SOD	SOS	SSF	SSY	STF
STI	*STO	STT	SZR	TER	THO	TOL	TON	TSC	TUN	UEI	UFI
UOZ	USI	UTL	VET	VFI	VNI	VSV	WEI	-WEN	YUG	ZON	

## Database of Zeolite Structures

[IZA-SC](#)

[Framework Type](#)

[References](#)

[Powder Patterns](#)

[Building Schemes](#)

[Disordered Structures](#)

[Other Links](#)

[Credits](#)

## Other Zeolite Database Links

**There are some zeolite-related databases on other websites that may be of interest:**

[AIPO Structures](#)

database of over 200 aluminophosphate structures

maintained by  
Y. Li, J. Yu and R. Xu  
Jilin University, Changchun, China

[AIPO Syntheses](#)

database of over 1600 aluminophosphate syntheses

maintained by  
J. Li, J. Yu and R. Xu  
Jilin University, Changchun, China

[Hypothetical Zeolites](#)

database of hypothetical zeolite structures

maintained by  
M.D. Foster and M.M.J. Treacy  
Arizona State University

[RCSR](#)

reticular chemistry structure resource, including a searchable database of 3-periodic nets

maintained by  
M. O'Keeffe  
Arizona State University

# ICSD—Inorganic Crystal Structure Database

➤ Produced cooperatively by achinformatiionszentrum Karlsruhe (FIZ), Germany, and the US Institute of Standards and Technology (NIST) .

➤ All collected from journals

➤ A comprehensive collection of more than 60,000 crystal structure entries for inorganic materials.

➤ **Zeolite** entries: 1648.

Sample  
ICSD  
record

\*data for ICSD #6271

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Coll Code 6271

Rec Date 1980/01/01

Mod Date 2000/12/16

Chem Name Cobalt Sodium Tecto-alumosilicate \*

Structured Co<sub>4</sub> Na<sub>4</sub> (Si<sub>12</sub> Al<sub>12</sub> O<sub>48</sub>)

Sum Al<sub>12</sub> Co<sub>4</sub> Na<sub>4</sub> O<sub>48</sub> Si<sub>12</sub>

ANX ABC6X12

Min Name Zeolite A

Min Origin Zeolite A (Co-exchanged, dehydrated) - synthetic

Min Group Zeolite

D(calc) 1.65

Formula Wt 1756.424

Title Crystal structures of dehydrated partially cobalt(II)exchanged zeolite A ...

Author(s) Riley, P.E.;Seff, K.

Reference Inorganic Chemistry (1974), 13, 1355-1360

Unit Cell 12.087(5) 12.087(5) 12.087(5) 90. 90. 90.

Vol 1765.86

Z 1

Space Group P m -3 m

SG PM3-M

SG Number 221

Cryst Sys cubic

Laue Class m3-m

Pearson cP80

Wyckoff m k i h g2

R Value 0.072

Sample  
ICSD  
record,  
continued

Symmetry

1	0	0	0	1	0	0	1	0	0	-1	0	0
2	0	0	1	0	0	1	0	0	0	0	0	-1
3	0	1	0	0	0	0	0	1	0	0	-1	0
4	0	0	0	1	0	1	0	0	0	0	-1	0
5	0	0	1	0	0	0	0	1	0	-1	0	0
6	0	1	0	0	0	0	1	0	0	0	0	-1
7	0	0	0	1	0	0	-1	0	0	1	0	0

.....

Red Cell P 12.087 12.087 12.087 90 90 90 1765.857

Trans Red 1.000 0.000 0.000 / 0.000 1.000 0.000 / 0.000 0.000 1.000

Comments R(isotropic)=0.086

Total SOF on at least one site differs from unity (SOF < 0.997 resp. SOF > 1.003)

Compound with mineral name: Zeolite A

Structure type : Zeolite-A

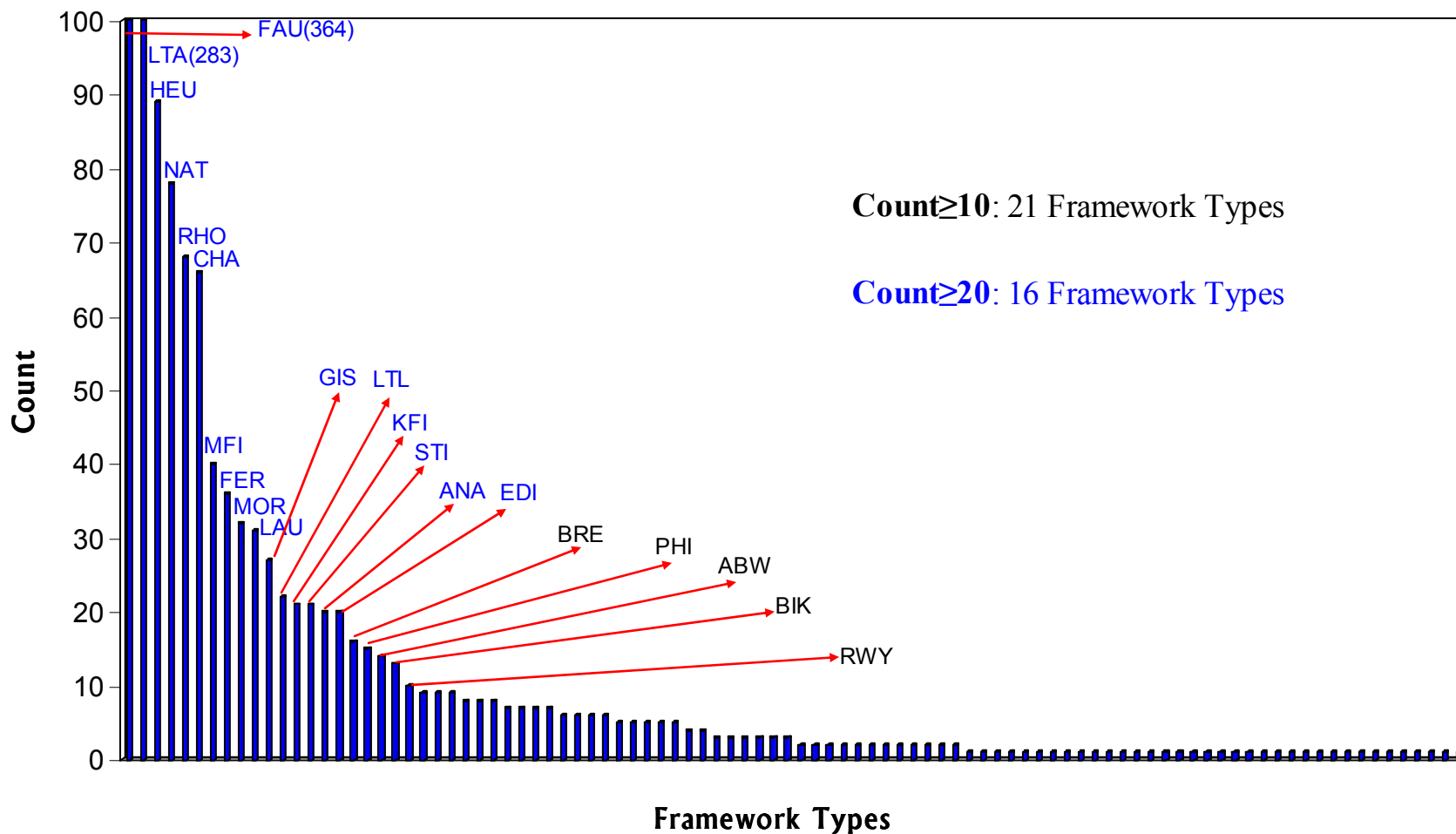
Atom #	OX	SITE	x	y	z	SOF	H
Si 1	+4	24 k 0	0.183(1)	0.367(1)	0.5	0.5	0
Al 1	+3	24 k 0	0.183(1)	0.367(1)	0.5	0.5	0
O 1	-2	12 h 0	0.201(3)	0.5	1.	1.	0
O 2	-2	12 i 0	0.298(2)	0.298(2)	1.	1.	0
O 3	-2	24 m 0.115(1)	0.115(1)	0.323(1)	1.	1.	0
Co 1	+2	8 g 0.200(2)	0.200(2)	0.200(2)	0.5	0.5	0
Na 1	+1	8 g 0.158(2)	0.158(2)	0.158(2)	0.5	0.5	0

\*end for ICSD #6271

# Zeolites in ICSD

- Min Group: Zeolite--1648 entries.
- Chem Name: 822
- Min Name: 289
- Framework Type Codes (FTC): 96

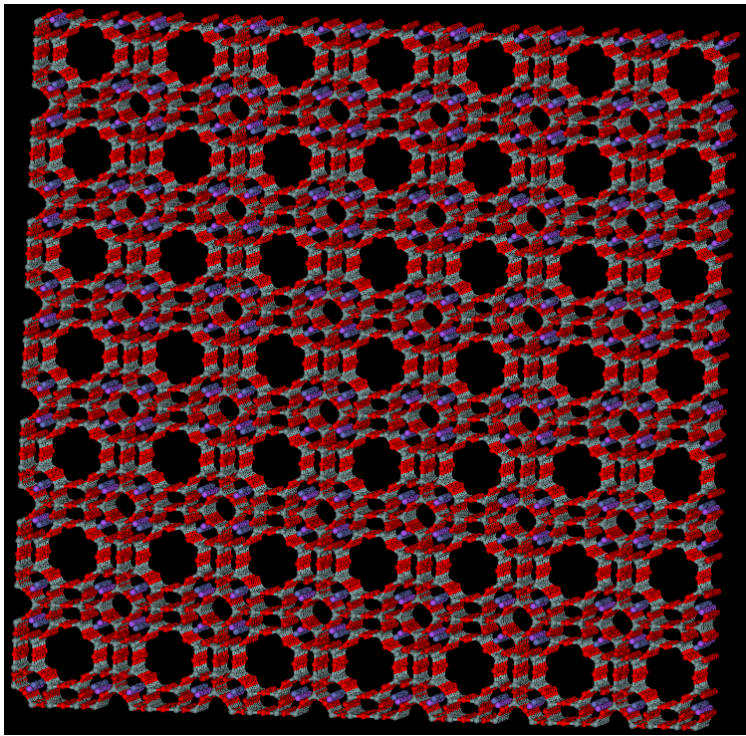
# Framework types of the zeolites in ICSD



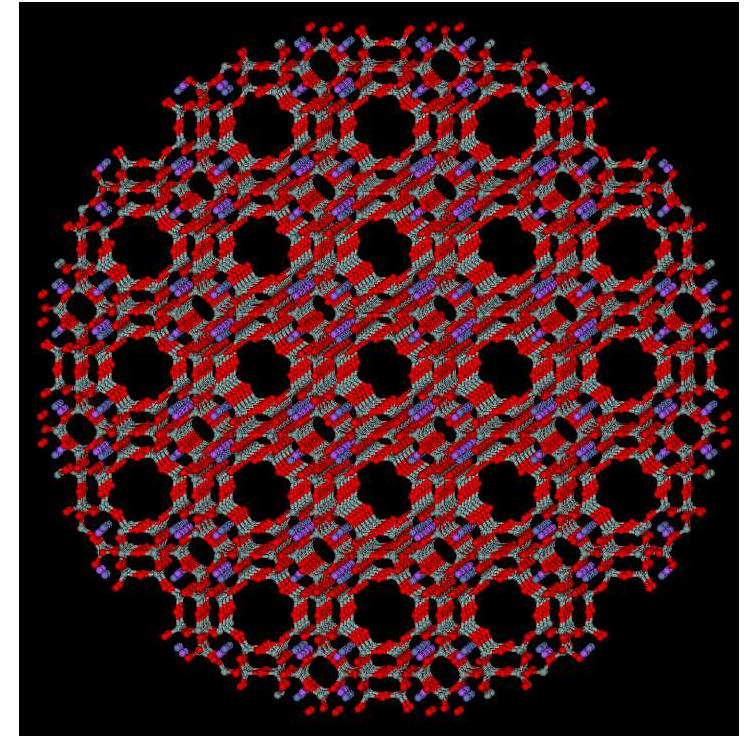
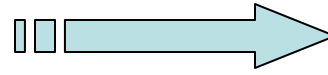
# Data treatment

- Asymmetric unit
  - the smallest portion of a crystal structure to which crystallographic symmetry can be applied to generate one unit cell.
- Generate the unit cell
  - Symmetry operations
  - Space groups
- Expand the unit cell to supercells
  - Translation of unit cell to multiples in 3-dimension

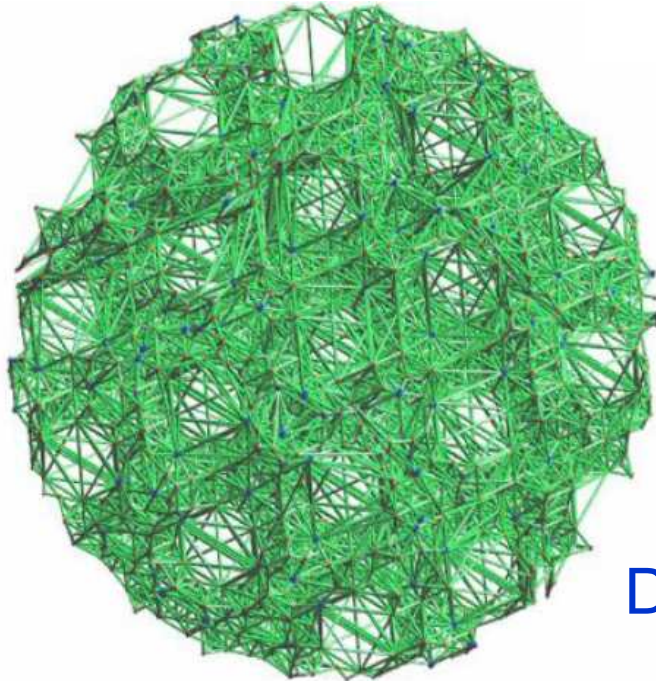
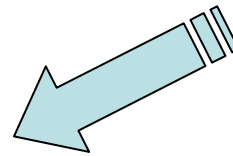
# ICSD# 6271, zeolite A



7x7x7  
supercell



spherical cut with  
radius 35.32 Å



Delaunay tessellation

# CMaSC model of zeolite classification

- Computational topological analysis
  - Delaunay Tessellation
- Machine learning, i.e. algorithms in WEKA
- Classification
  - Random Forest algorithm
- Zeolite Structure Predictor (ZSP) is a classifier
  - Classifies into 40 framework types
  - **Correctly classifies 95.24% of the zeolites**
  - Random classification yields about **5% !!!**