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CHEMICAL NOMENCLATURE AND FORMULATION OF COMPOSITIONS OF SYNTHETIC AND NATURAL ZEOLITES

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The designation of natural zeolites has followed the traditional pattern of mineralogy and
has been developed into a system comprising about seven groups each with a number of
members, as described, for example, by Meier (in Molecular Sieves, Society of Chemical
Industry, London, 1968, p. 10). The development of molecular sieves in technology and
industry has, however, resulted in the synthesis of a number of structures which have no
natural counterparts. Further, a large number of novel zeolitic aluminosilicate frameworks
can be constructed, at least some of which will probably be synthesised in the future.

The nomenclature of the synthetic variants and of novel synthetic zeolites has so far been
very confused, because listing has been different in each laboratory. To introduce order
into this complicated situation, a method for the systematic description of synthetic
zeolites is proposed, which can be used equally well for natural zeolites. The aims of the
formula must be:

(1) to give as full information as possible;

(2) to provide an overall formula which is unique;

(3) not to become cumbersome; and

(4) where desired, to maintain the practice of using a short group of characters, e.g., A,
     L, P, which by themselves could be used in phase diagrams, isotherms, etc.

The chemistry of zeolites includes the following aspects, about which the formula might
provide information, at least briefly:

(1) cation exchange;

(2) isomorphous replacement;

(3) structural type;

(4) lattice defects of chemical types.

In what follows we consider these aspects in relation to a formula.

1. STRUCTURAL TYPE AND CATION COMPOSITION

Naturally occurring zeolites are aluminosilicates with tectosilicate anionic frameworks so
that O: (Al + Si) = 2:1. The frameworks acquire their negative charge by substitution of
some Si^{IV} by Al^{III}. The negative charge is neutralised by cations and the
frameworks are sufficiently open to contain, under normal conditions, mobile water molecules
which may be removed, usually reversibly, by heat and/or evacuation. Synthetic zeolites
have the same properties except that in some the Al and Si have been replaced wholly or in
part by other elements such as Ga and Ge.

The following recommendations and suggestions are made concerning structural type and cation composition:

(a) A structural type designation is required to give the topology of the anionic framework. A list of type designations for some zeolites of known structures is given in Table 1. Three capital italic letters are the normal designation except for well-known structures for which letters have already been accepted (e.g., zeolite L = *L*; zeolite A = *A*; zeolite ZK-5 = *ZK5*). Structural type designations include all chemical and structural variants of a given framework topology. For instance, *ANA* is the designation for both analcime and wairakite. Other examples appear in Table 1.

(b) New structural type designations should be subject to approval (like new mineral names) by an official committee. New designations must not be introduced without sufficient evidence based on a structure determination. Designations of hypothetical frameworks should be clearly distinguished from those of established structural types by a special superscript such as an asterisk. Such designations should not be included in the table of accepted designations and under no circumstances should they be means for establishing priority.

(c) Either in listing the cations that were originally present, or in giving the cation composition after ion exchange, these cations should be given in alphabetical order.

(d) The formula will normally represent the composition corresponding with one electro-chemical equivalent of the cations.

(e) For many purposes the full composition is not needed. As an example, a synthetic zeolite L may be considered. The cations present in this zeolite as originally synthesised were K^+ and Na^+. This is denoted by (K,Na) and if only structural type and cations present are required, the zeolite is written as

$$(K,Na)-L$$
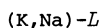
The brackets are omitted if only one kind of ion is present. If the K^+ and Na^+ contents have been determined, the above expression becomes
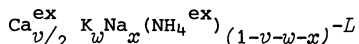
$$K_x Na_{(1-x)}-L$$
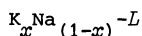
where the comma and brackets are not required.

(f) If the K^+ and Na^+ are partially exchanged by other ions such as NH_4^+ and Ca^{2+} and it is desired to indicate that an exchange has occurred, the composition is given as

$$(Ca^{ex},K,Na,NH_4^{ex})-L$$
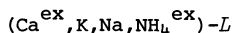
or, for known proportions of the cations,

$$Ca^{ex}_{v/2} \, K_w Na_x (NH_4^{ex})_{(1-v-w-x)}-L$$

This method of expressing cation compositions readily includes the naturally occurring zeolites. Thus for a phillipsite in which the ions present are, say, unknown amounts of Ca, K and Na, one writes

$$(Ca,K,Na)-Phillipsite$$
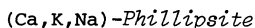
or, in terms of the structural type designation of Table 1,

$$(Ca,K,Na)-PHI$$
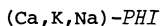
(g) It can happen that a zeolite having a novel framework topology is first obtained and named as a synthetic compound, but is subsequently found to occur naturally and is given a mineralogical name. In this case the mineralogical name should be used to indicate the topology.

(h) Some synthetic zeolites and variants of natural zeolites contain nitrogenous ions, such as alkylammonium ions. Thus for zeolite *A* with Na^+ and tetramethylammonium (NMe_4^+) ions in the structure, one has

$$(Na, NMe_4)-A$$

or, if the cationic composition is known,

$$Na_{(1-x)} (NMe_4)_x-A$$
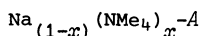
Similar considerations apply when other organic cations, such as alkylsulphonium or alkyl-phosphonium, are present.

(*i*) Tetramethylammonium or other alkylammonium ions can hydrolyse under hydrothermal conditions. Thus NMe_4^+ may yield

$$NHMe_3^+, \ NH_2Me_2^+, \ NH_3Me^+ \text{ and } NH_4^+$$

in unknown proportions in the zeolite, but representing in all x equivalents of nitrogen. The exact composition of the mixture of organic ions in the zeolite is

$$\sum_{n=0}^{4} x_n NH_n Me_{(4-n)} \qquad \text{where} \qquad \sum_{n=0}^{4} x_n = x$$
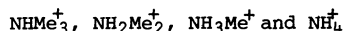
In standard chemical notation, however, such a sum in a formula is written as though it were the product

$$\prod_{n=0}^{4} \left(NH_n Me_{(4-n)} \right) x_n$$

and so for a sample of zeolite A containing sodium and the above alkylammonium ions one has

$$Na_{(1-x)} \prod_{n=0}^{4} \left(NH_n Me_{(4-n)} \right) x_n \ -A$$

When the individual values of the x_n are not known but only the sum $\sum_{n=0}^{4} x_n = x$ the composition becomes

$$Na_{(1-x)} \left(\prod_{n=0}^{4} NH_n Me_{(4-n)} \right) x \ -A$$

while if x is not known, the composition is given as

$$\left(Na, \prod_{n=0}^{4} NH_n Me_{(4-n)} \right) \ -A$$

For convenience it has been customary to replace

$$\prod_{n=0}^{4} \left(NH_n Me_{(4-n)} \right) x \quad \text{by } N_x \text{ so that the composition } N_x Na_{1-x} \ -A \text{ denotes a sample of } A \text{ in}$$

which there are x equivalents of nitrogen. In this case the meaning of N_x should be given in the text, as "x equivalents of nitrogen distributed among the alkylammonium ions which are present in unknown proportions".

2. ISOMORPHOUS REPLACEMENTS IN THE ANIONIC FRAMEWORKS AND FRAMEWORK COMPOSITIONS

Such replacements as

$$Na, Al \rightleftharpoons Si$$

$$Ba, 2Al \rightleftharpoons 2Si$$
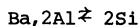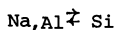
are common among naturally occurring and synthetic zeolites. They arise as a result of differing synthesis conditions, but after synthesis cannot be effected directly. Such replacements are reflected in the Si:Al ratio of the zeolite. Through synthesis one may also have other isomorphous replacements such as

$$Al \rightleftharpoons Ga$$

$$Si \rightleftharpoons Ge$$

As with other tectosilicates, zeolite frameworks are formed from tetrahedra MO_4 where M may include such atoms as Al, Ga, Fe, Ge and Si. A central tetrahedron is linked with each of four other tetrahedra by sharing its four oxygens, one between each pair of tetrahedra. As a consequence, tetrahedra of $Ge^{IV}O_4$ or $Si^{IV}O_4$ contribute no nett charge to the framework and tetrahedra of $Al^{III}O_4$, $Ga^{III}O_4$ or $Fe^{III}O_4$ each contribute one negative charge. On the other hand, if $P^V O_4$ tetrahedra were incorporated into the tectosilicate framework in the same way, they would each contribute one positive charge to the framework.

Suppose we have a framework containing:

p mol of Al

q mol of Ga

r mol of Ge

and s mol of Si

Then for one electrochemical equivalent of cations (compare Section 1(d)) , the corresponding amount of anionic framework must be characterised by

$$p + q = 1 \qquad\qquad\qquad (1)$$

The proportions p, q, r and s in the above example must be established by analysis. The amount of oxygen in the framework must then be $2z$ where

$$z = p + q + r + s \qquad\qquad\qquad (2)$$

The following recommendations and suggestions arise from isomorphous replacement of framework forming atoms:

(a) The framework forming atoms should be listed in alphabetical order, except for oxygen which should always be given last in the framework composition.

(b) The amounts of the framework forming atoms in the formula must correspond with one electrochemical equivalent of exchangeable cations in accord with equation (1) above. Alternatively, if the unit cell is known, the unit cell composition may be given.

(c) The framework composition should be placed in square brackets. Thus the composition of a hypothetical variant of phillipsite type containing K and Na and the framework atoms Al, Ga, Ge and Si in the proportions given by equation (2) is represented in its water-free condition as

$$K_x Na_{(1-x)} \left[(Al_p Ga_q Ge_r Si_s) O_{2z} \right] \text{-}PHI$$
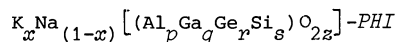
If the unit cell compostition is desired, it is necessary only to multiply everything except the structural type designation by the number of equivalents of cationic charge per gramme unit cell. If the elements present are known but not their amounts, the above formula becomes

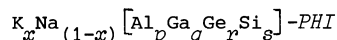$$(K,Na) \left[(Al,Ga,Ge,Si)_z O_{2z} \right] \text{-}PHI$$
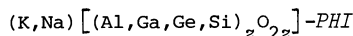
z corresponds with one electrochemical equivalent of anionic framework.

(d) Since the oxygen content is fixed for any tectosilicate framework once the amounts of the other framework forming atoms are known (see equation (2)), formulae such as

$$K_x Na_{(1-x)} \left[(Al_p Ga_q Ge_r Si_s) O_{2z} \right] \text{-}PHI$$
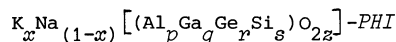
may conveniently be abbreviated to

$$K_x Na_{(1-x)} \left[Al_p Ga_q Ge_r Si_s \right] \text{-}PHI$$

while if x, p, q, r and s are not known, the abbreviation becomes

$$(K,Na) \left[Al,Ga,Ge,Si \right] \text{-}PHI$$
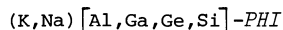
The above scheme can, if desired, include other tectosilicates such as felspars and felspathoids.

3. ZEOLITIC WATER

If y molecules of water are found by analysis to be associated with one electrochemical equivalent of exchangeable cations, then the composition of the hypothetical synthetic phillipsite of the previous section is

$$K_x Na_{(1-x)} \left[(Al_p Ga_q Ge_r Si_s) O_{2z} \right] yH_2O \text{-}PHI$$
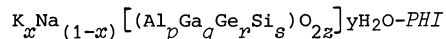
4. SPECIAL NAMES AND LISTINGS

It is customary in the literature to list the synthetic zeolites prepared in any given laboratory under letters or under special names. Names such as Zeolon for a synthetic mordenite-type zeolite are trade names and as such should not be used in formulating compositions. On the other hand, listings by letters such as those referred to in Section 1(a) (e.g., zeolites A, X, Y, L, Na-P and A) are very well established. In cases where there is no natural counterpart, the letter designation serves naturally as the structural type designation, indicating the known framework topology. A disadvantage of listing synthetic zeolites by letters is that zeolites having the same framework topology, made in different laboratories, have been listed with two or more different letters (see Table 2); and that the same letter has

been used in different laboratories to list zeolites of differing topologies.

It has been suggested, on the one hand, that particular letter or other designations should be abandoned whenever the structural type is known to correspond with that of a naturally occurring species. On the other hand, it has been pointed out that the synthetic phases often represent variants or sub-species of the structural type sufficiently distinct to require special recognition, such as may be conferred on them by the special designation. For example, zeolite Na-P has been found to be based on the gismondine structure but its X-ray powder pattern is so different from that of gismondine that they would not be easily recognised as related species. The differences are greater than those between pairs of natural compounds such as nosean and sodalite to which mineralogists have given separate names and identities.

The occurrence of synthetic variants or sub-species of a structural type may also rest on substantial differences in composition, at least as large as those distinguishing harmotome and phillipsite, for example. In the zeolite field sub-species are much too frequent to be ignored. The recommended way of allowing for sub-species is to use the special designations alongside the structural type so that Na-P, for instance, would be written as

Na - P, *GIS*

to indicate that this is the variant of the gismondine structural type which has been termed Na - P.

The use of special designations should imply a significant difference between the type-compound and the sub-species or variants in structure or composition, and hence in properties. The full chemical formula corresponding with Na - P, *GIS* would be

$$\mathrm{Na}_{1.0}[\mathrm{Al}_{1.0}\mathrm{Si}_{s}\mathrm{O}_{(2+2s)}]y\mathrm{H_2O} - \mathrm{P}, \textit{GIS}$$
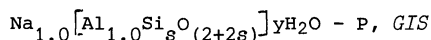
where s and y are established by analysis.

5. CRYSTALLOGRAPHIC INFORMATION

Details of the unit cell and structure must be given separately from the formula, and can be obtained readily from the literature once the structural type *GIS*, *PHI*, etc. is indicated in the formula. The crystal symmetry of the structural type could be indicated by a subscript to the structural type designation. However, there seems little advantage in this, as such information is contained in the structural type designation. Also, sub-species, though based on the same framework, need not have the same symmetry as the type species. It is recommended that these symmetry symbols should not be included.

6. LATTICE MODIFICATION BY CHEMICAL MEANS

Lattice modification of zeolites may be of the following kinds:

(i)   decationation;

(ii)   decationation plus dehydroxylation;

(iii) dealumination; and

(iv)   dealumination plus dehydroxylation.

In decationation metallic cations are replaced by hydrogen, largely as silanol groups. This process is usually effected by heating the ammonium exchanged form of the zeolite. A fully decationated zeolite has been termed a hydrogen zeolite. For example, the hydrogen form of zeolite Y becomes

H - Y, *FAU*

Stronger heating brings about loss of silanol water from the hydrogen zeolite, this water loss being termed dehydroxylation. A range of products may be formed by combined decationation plus dehydroxylation in which, while much of the regularity of the parent lattice is retained, there are also various changes.

Again, for example by suitable treatment with acid, aluminium may be removed from silica-rich zeolites such as mordenite or clinoptilolite wholly or in part without major changes in the crystalline pattern given by X-ray diffraction. Heating such dealuminated zeolites also liberates chemically bound water, as a dehydroxylation process. Changes occur which, like those in decationation plus dehydroxylation, are not fully understood and may yield a range of modified frameworks.

The complexity of these changes makes it difficult to include them in compositional formulae. It is reasonable to continue to refer to the decationated zeolite as H-zeolite, but no formal

recommendations are made about this or the other processes except that the modified zeolites should continue to be termed 'decationated', 'dehydroxylated' or 'dealuminated' or combinations of these terms, as necessary.


7. INTERCALATION

The guest molecules normally present in natural or synthetic zeolites are water molecules, which are driven off during activation of the zeolite. However, it is possible to have non-volatile intercalated guest species which may substantially modify the molecular sieve behaviour, the stability and/or the catalytic properties of the zeolite. It may, therefore, be important to be able to include these impurities, where they are known, in the formula.

Impurities of this type may be incorporated adventitiously and largely unavoidably during synthesis (additional alkali, for example in cancrinite hydrate; or silicate or aluminate); or they may be introduced afterwards by impregnation of the crystals by aqueous or molten salts (e.g., zeolites X, Y or A); or from vapours of volatile salts. This impregnation may be followed by chemical breakdown to incorporate metals (e.g., $PtCl_4$ into zeolites X or Y followed by heating or reduction to deposit Pt atoms in the zeolite).

The means of specifying the presence of intercalated material is relatively straightforward: the guest impurity can be considered in the same way as the zeolitic water, even though it may not be easy to remove the guest. Thus a typical decationated zeolite Y, with intracrystalline Pt atoms can be written

$$H\left[(Al_{1.0}Si_s)O_{(2+2s)}\right]yH_2O, \text{ wPt} - Y, \textit{FAU}$$
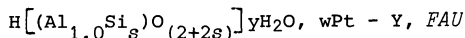
If, however, some of the Pt migrates out of the crystal and forms Pt metal crystallites externally, the formula becomes

$$xPt + H\left[(Al_{1.0}Si_s)O_{(2+2s)}\right]yH_2O, \text{ (w-x)Pt-Y, } \textit{FAU}$$
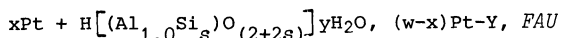
8. CONCLUSION

A reasonable formulation can be made of synthetic zeolite compositions in the way described. Not all the aspects of nomenclature which have been indicated may be needed at any one time so that quite brief formulae may be used. However, those aspects which are needed should be introduced in the order outlined. This sequence is illustrated in Table 3 for a typical formula. Table 1 gives structural type designations for a range of zeolites, and Table 2 illustrates abbreviated formulae for a number of typical synthetic zeolite preparations.

TABLE 1. Structure type designations of known zeolite frameworks

Species	Structure type designations	Species	Structure type designations
Analcime, Wairakite	*ANA*	Merlinoite	*MER*
Laumontite, Leonhardite	*LAU*	Yugawaralite	*YUG*
Natrolite, Mesolite, Scolecite	*NAT*	Heulandite, Clinoptilolite	*HEU*
Thomsonite, Gonnardite	*THO*	Stilbite, Stellerite, Barrerite	*STI*
Edingtonite	*EDI*		
Sodalite hydrate, Tugtupite	*SOD*	Brewsterite	*BRE*
		Mordenite	*MOR*
Cancrinite hydrate	*CAN*	Dachiardite	*DAC*
Gmelinite, Na-S	*GME*	Epistilbite	*EPI*
Chabazite, Herschelite, K-G	*CHA*	Ferrierite	*FER*
		Zeolite Li-A(BW)	*ABW*
Erionite	*ERI*	Bikitaite	*BIK*
Offretite	*OFF*	Faujasite, X, Y, etc.	*FAU*
Mazzite	*MAZ*	Zeolite A, ZK-4, etc.	*A*
Losod	*LOS*	Zeolite ZK-5;	*ZK5*
Zeolite L; Ba-G, *L*	*L*	Species P & Q	
Phillipsite, Harmotome	*PHI*	Paulingite	*PAU*
Gismondine, Na-P, Linde B	*GIS*	Zeolite RHO	*RHO*

TABLE 2. Examples of synthetic zeolites

Group name	Specific member	Previous designations	Reference	Abbreviated formulae
Faujasite	Faujasite	Na$_2$X	USP 2,882,244	Na[Al$_{1.0}$Si$_{1.25}$]-X,*FAU*
		Zeolite type X	Breck et al. JACS 1956	Na[Al$_{1.0}$Si$_{1.25}$]-X,*FAU*
		Na-R	Barrer et al. JCS 1959	Na[Al$_{1.0}$Si$_{1.20}$]-R,*FAU*
		Na-R	Barrer et al. JCS 1959	Na[Al,Ge]-R,*FAU*
		Na-R	Barrer et al. JCS 1959	Na[Ga,Ge]-R,*FAU*
		N-R	Barrer et al. JCS 1961	N[Al,Si]-R,*FAU*
		Na-X	Zhdanov. Zeo.Conf. 1967	Na[Al,Si]-X,*FAU*
		N-X	USP 3,306,922	N[Al,Si]-X,*FAU*
		Na-F	Taylor and Roy.Am.Min.1964	Na[Al,Si]-F,*FAU*
		Zeolite type Y	USP 3,130,007	Na[Al$_{1.0}$Si$_{2.50}$]-Y,*FAU*
	Zeolite A	Zeolite type A	Breck et al. JACS 1956	Na[Al$_{1.0}$Si$_{1.0}$]-*A*
		Na$_2$A	USP 2,882,243	Na[Al$_{1.0}$Si$_{1.0}$]-*A*
		Na-Q	Barrer et al. JCS 1959	Na[Al$_{1.0}$Si$_{1.0}$]-Q,*A*
		Na-A	Zhdanov Zeo. Conf. 1967	Na[Al,Si]-*A*
		ZK-4	Belg. Pat. 621,841	NMe$_4$[Al$_{1.0}$Si$_{1.70}$]-ZK4,*A*
		Na,Me$_4$α	Fr. Pat. 1,364,562	(Na,NMe$_4$)[Al,Si]-α,*A*
		Na-Q	Barrer et al. JCS 1959	Na[Al,Ge]-Q,*A*
		Na-Q	Barrer et al. JCS 1959	Na[Ga,Ge]-Q,*A*
		N-A	USP 3,306,922	N[Al,Si]-*A*
Natrolite	Thomsonite	Ca-I	Barrer et al. JCS 1961	Ca[Al,Si]-I,*THO*
		Na-V	Barrer et al. JCS 1959	Na[Al,Ge]-V,*THO*
		Na-V	Barrer et al. JCS 1959	Na[Ga,Ge]-V,*THO*
Phillipsite	Harmotome	Ca-L	Barrer et al. JCS 1961	Ca[Al,Si]-L,*PHI*
		Ba-M	Barrer et al. JCS 1964	Ba[Al,Si]-M,*PHI*
	Phillipsite	Na,K-M	Barrer et al. JCS 1959	(Na,K)[Al,Si]-M,*PHI*
		K-M	Barrer et al. JCS 1956	K[Al,Si]-M,*PHI*
		KW	USP 3,012,853	K[Al,Si]-W,*PHI*
	Zeolite Na-P	Na-P1	Barrer et al. JCS 1959	Na[Al,Si]-P1,*GIS*
		Na-P2	Barrer et al. JCS 1959	Na[Al,Si]-P2,*GIS*
		Na-P3	Barrer et al. JCS 1959	Na[Al,Si]-P3,*GIS*
		Cubic phillipsite	Hoss and Roy. Beitr. Mineral Petrogr. 1960	Na[Al,Si]-P1,*GIS*
		NaB	USP 3,008,803	Na[Al,Si]-B,*GIS*
		Zeolite B	Shara. Am.Min. 1959	Na[Al,Si]-B,*GIS*
		Pc,Pt,Po	Regis et al. J.Phys.Chem.1960	Na[Al,Si]-P,*GIS*
Mordenite	Mordenite	Na-D	Barrer. JCS 1948	Na[Al$_{1.0}$Si$_{5.0}$]-D,*MOR*
		Na-M	Senderov. Geochem. 1963	Na[Al,Si]-M,*MOR*
		Md	Zhdanov. Zeo.Conf. 1967	Na[Al,Si]-Md,*MOR*
Chabazite	Gmelinite	Na-S	Barrer et al. JCS 1959	Na[Al,Si]-S,*GME*
		Sr-F	Barrer et al. JCS 1964	Sr[Al,Si]-F,*GME*
		Ca,N-G	Barrer et al. JCS 1961	(Ca,N)[Al,Si]-G,*GME*

TABLE 3. A typical formula and its significance

$$H_{0.9}Na_{0.05}(NH_4)_{0.05}[(Al_{0.6}Ga_{0.4}Ge_{0.53}Si_{0.80})O_{4.66}]yH_2O, 0.6Pt - Y, \mathit{FAU}$$

Structural Type

Variant or Sub-Species

Amount and Type of Guest Species

Framework Composition and Extent of Isomorphous Replacements

Cation Content Remaining after Exchange and Other Treatments (Decationation, etc.)

Extent of Decationation