A NUMERICAL ANALYSIS OF ZEOLITE STRUCTURES [1]

III. "STRUCTURAL" AND CHEMICAL COMPOSITIONS: A DISCUSSION IN RELATION TO THE CLASSIFICATION OF NATURAL ZEOLITES

BY

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ABSTRACT

The previously defined relations between the water, Al and cavity cation compositions are examined for about 20 refined structures of natural zeolites, all characterized by Si or Al-centered oxygen tetrahedra. From an analysis of the numbers of O atoms with specific coordination spheres within zeolite structures, a relation between the Si content, the water content and the cavity cation coordination is established. The groups of the classification of natural zeolites by *Gottardi and Galli* are then defined with simple equations expressing the "structural" composition of zeolites. From a chemical point of view, one distinguishes the *Al-rich* from the *Si-rich* zeolites on one side, and, on the other side, zeolites with *a low water content* from those with *a high water content*. "Structural" composition and chemical composition are thus shown to be interrelated.

Keywords: zeolites, structural chemistry, oxygen coordination numbers, classification.

1. INTRODUCTION

In the first two parts of this series of three papers, we analysed numerical relationships for zeolite structures on the basis of a theoretical model which takes account of the coordinations of the O atoms. It was shown that the cavity cation coordination is essential for the valence equilibrium also within these structures. In the ideal case of this model, fields for "structural" compositions for zeolites were defined (Engel, 1989). The limiting conditions for these fields are summarized in the left column of table 1. Thus, for zeolite structures with a theoretical composition
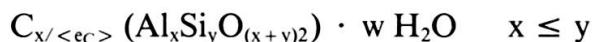
$$C_{x/<e_C>} (Al_x Si_y O_{(x+y)2}) \cdot w \, H_2O \qquad x \leq y$$

[for which $e_C = 1$ for C = Li^{1+}, Na^{1+}, K^{1+} ... ; $e_C = 2$ for C = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} ...; $<e_C>$: mean valence electron number per cavity cation (C) — see appendix A in Engel, 1988], the mean number of water molecules per Al atom bound to one cavity cation (r), varies between one and four ($1 \leq r \leq 4$) (table 1). Further, there are at least, on average, two O atoms whose sum of the cationic bond strengths is inferior to 2.0 valence units ("valence deficient", and therefore possible "acceptors" for H atoms), which, linked to the Al atom, form part of each of these O tetrahedra (table 2 in Engel, 1989); for each of these O atoms, there are, on average, one or two C-coordinated water oxygens ($1/2 \leq V \leq 1$; table 2 in Engel, 1989). Finally, a limit between zeolites with a "low water content" and those with a "high water content" was defined in terms of the mean composition of the cavity cation polyhedron, which falls within $1 \leq r \leq 2$ (table 1). The mean composition of the cavity cation polyhedron is expressed with ξ (mean number, per cavity cation, of water molecules

TABLE 1.

Limiting conditions for zeolites according to the water, Al and cavity cation (C) contents expressed in terms of "structural" composition or chemical composition.

1. "Structural" parameters (compare table 2, Engel, 1989)	2. The water composition per Al atom (w/x) and $<CN_C>/<e_C>$ (compare fig. 2)	3. The Al (x) and water (w) compositions (compare fig. 4)	4. The cavity cations ($1/<e_C>$) and water (w/x) compositions per Al atom (compare fig. 3)
The number of the C-coordinated water molecules (r) per Al atom varies between 1 and 4. $1 \leq r \leq 4$	For the minimal value of r: r=w/x; for its maximal value, one estimates r ≈ w/x, thus $1 \leq w/x \leq 4$	$\boxed{x \leq w \leq 4x}$	
The minimal fraction of the mean cavity cation polyhedron built of ($\xi/<CN_C>$) is for $e_C/<CN_C> < 1/6$: $(\xi/<CN_C>)_{min} = 1/7$	As (ξe_C) = r (equ. (6) in Engel, 1988) and for r ≈ w/x: *minimal limit for w/x:* $\boxed{w/x = 1/7(<CN_C>/e_C)}$		
For $e_C/<CN_C> \geq 0.25$ v.u.: the maximal value for this fraction is: $(\xi/<CN_C>)_{max} = 1$	*maximal limit for w/x:* $\boxed{w/x = <CN_C>/e_C}$		(see table below)

$\frac{w}{(x/<e_C>)}$	$(1/<e_C>)_{max}$ $=1$	$(1/<e_C>_{min})$ $=0.5$
w/x=1	1	2
w/x=2	2	4
w/x=4	4	8

The limit between zeolites with a high water content and zeolites with a low water content is given by:

$(i''+1)* = r$

for $e_C/<CN_C> < 1/6$ v.u.:

$\xi = <CN_C>/2 \cdot 2$ or $\qquad w/x = 1/2(<CN_C>/e_C) -2/e_C$
$\quad r = (<CN_C>/2-2)/e_C$

for $e_C/<CN_C> \geq 0.25$:

$\xi = <CN_C>/2$ or
$\quad r = (<CN_C>/2)/e_C$
valid for: $\qquad\qquad\qquad\qquad \boxed{w/x = 1/2<CN_C>/e_C} \qquad \boxed{x \leq w \leq 2x}$
$\quad 1 \leq r \leq 2$

* number of the so-called "overloaded" O atom per Al atom (see O coordination in table 4)

coordinated to one C atom, see equ. (6) in Engel, 1988) and $<CN_C>$ (mean coordination number of the cavity cations, detailed definition in appendix A in Engel, 1988).

The analysis of valence distribution within zeolite structures (Engel, 1989) failed in revealing the possible silicon content relative to the content of water molecules, situated in the cavities or channels within the framework of oxygen tetrahedra. This relationship is of particular interest for zeolites with a high water content. The more Si atoms are in the structure, the denser the tetrahedra framework will be and thus the less space is left for water molecules and cavity cations. As the cavity cation and Al contents are related ($x/<e_C>$ in the above theoretical formula, see also the appendix A of Engel, 1988), the less Al atoms (or more Si atoms) that, in a given structure, center the framework tetrahedra, the fewer cavity cations and the relatively more water molecules that should be "attracted" in this structure. There follows an
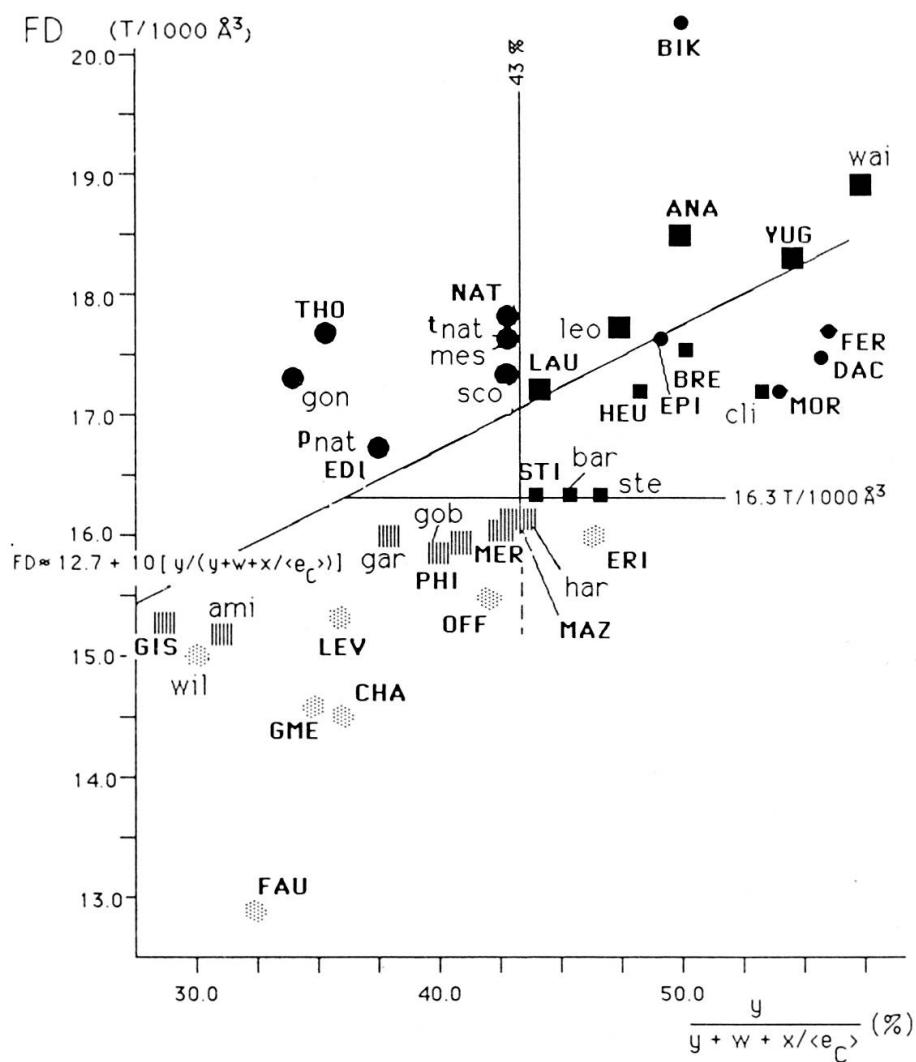

FIG. 1.

Framework density (FD) for natural zeolites as a function of the Si content (y) relative to the cavity cation and water compositions ($x/<e_C>$ and w). Signs are for the groups of the classification according to *Gottardi and Galli* (compare tables 3 and 5). Codes are according to the recommendations of the IZA.

increase in the number of the water molecule-cavity cations bonds, in such a way that the cavity cation coordination polyhedra may even be completely formed by water molecules.

In view of this, the relation between the stoechiometric composition and the coordinations of the chemical constituents within zeolite structures should be a function of the geometrical arrangement of the Si or Al-centered tetrahedra, which is the way to classify silicate structures. Accordingly, for natural zeolites, Gottardi and Galli (1985) distinguish six groups: the *fibrous zeolites,* the zeolites with *singly connected 4-ring chains,* the zeolites with *doubly connected 4-ring chains,* those with *6-rings,* the zeolites of the *Mordenite group* and those of the *Heulandite group.* In fig. 1, the relation between the density of the structure (we use here the framework density (FD) defined by Meier and Olson, 1988, as the number of T atoms per 1000 $Å^3$) and the percentage Si content relative to the total water and cavity cation contents is shown with examples for natural zeolites classified within the above groups. The limits given in this figure are discussed in sections 4 and 5 of this paper where a global review for natural zeolites in relation to the chemical composition is presented.

The first step in this discussion is to show how the model, on which this analysis is based (see the preceding papers of this series), and the derived limiting conditions, which concern only the water, Al and cavity cation compositions (table 1), are verified for zeolite structures. For this purpose, about 20 refined structures of natural zeolites are examined. An analysis of *the oxygen coordination numbers* is presented afterwards. It gives an estimation of the Si content in relation to the water content. Since some of the O atoms, bound to 2 Si atoms, are also observed to be "acceptor" for H atoms, an analysis of the possible O "acceptors" is consequently presented. The limits between the groups of the classification are finally discussed in terms of "structural" and chemical compositions.

2. THE WATER, AL AND CAVITY CATION COMPOSITIONS OBSERVED IN ZEOLITE STRUCTURES

In table 1, the "structural" conditions for zeolites defined previously (table 2 in Engel, 1989) as a function of the mean composition of the cavity cation polyhedra are expressed in terms of the water, Al and cavity cation compositions. The relation between the mean number, per Al atom, of water molecules coordinated to one cavity cation (r) and the water content per Al atom (w/x) is written $w/x = r$ for short. In the two right columns of table 1, only the stoechiometric compositions are considered; notice that, in these columns, a lot of information is lost, since the cavity cation coordinations are no longer included.

TABLE 2.

The identifiers for the coordination of the O atoms (see coordinations in table 4) calculated from the structure refinements of some natural zeolites.

mineral [reference]	k	l+i"	i'+g	r	s	$<CN_C>^a$	$<e_C>^b$	
Zeolites with a low water content								
thomsonite [1]N	0	2	0.4+1.6	1.2*	-	8	1.67	$Na_4Ca_8(Al_{20}Si_{20}O_{80})\ 24H_2O$
gonnardite [2]	0.21	1.53	1.1+1.4	1.34*	-	8	1.2	$Na_{6.5}Ca_{1.5}(Al_{9.5}Si_{10.5}O_{40})\ 12.4H_2O$
mesolite [3]	1	1.67	0.7+1.67	1.33*	-	6.5	1.5	$Na_{16}Ca_{16}(Al_{48}Si_{72}O_{240})\ 24H_2O$
natrolite [4]N	1	1	2 + 1	1*	-	6	1.0	$Na_{16}(Al_{16}Si_{24}O_{80})\ 16H_2O$
edingtonite [5]N	1	0	3 + 1	2	-	10	2.0	$Ba_2(Al_4Si_6O_{20})\ 8H_2O$
scolecite [6]N	1	2	2	1.5	-	7	2.0	$Ca_8(Al_{16}Si_{24}O_{80})\ 24H_2O$
analcime [7]N	2	0	4 + 0	1*	-	6	1.0	$Na_{16}(Al_{16}Si_{32}O_{96})\ 16H_2O$
laumontite [8]	2	2	2	≤2	-	≤8	2.0	$Ca_4(Al_8Si_{16}O_{48})\ ≤16H_2O$
bikitaite [9]	2	3	1	1	-	4	1.0	$Li_2(Al_2Si_4O_{12})\ 2H_2O$
wairakite [10]	2.19	2	2	1*	-	6	<2.0	$Ca_{7.2}(Na,K)_{1.2}(Al_{15.5}Si_{32.5}O_{96})\ 16H_2O$
yugawaralite [11]	4	2	2	2	-	8	2.0	$Ca_2(Al_4Si_{12}O_{32})\ 8H_2O$
Zeolites with a high water content								
amicite [12]	0	1	3	1.25*	0	6.75	1.0	$Na_4K_4(Al_8Si_8O_{32})\ 10(?11)H_2O$
gismondite [13]	0.44	1.11	2.98	2.33	0.07	6.5	2.0	$Ca_{0.92}(Al_{1.8}Si_{2.2}O_8)\ 4.3H_2O$
levyne [14]	2.0	1.36	2.64	≤2.42*	≤0.43	6.22	1.71	$NaCa_{2.5}(Al_6Si_{12}O_{36})\ 18H_2O$
phillipsite [15]	1.82	0.75	3.25	≤2.4*	≤0.3	9.74	1.38	$\sim K_2Ca_{1.5}Na_{0.4}(Al_{5.5}Si_{10.5}O_{32})\ 12H_2O$
harmotome [15]	2.4	0.48	3.52	≤2.4*	≤0.56	9.85	2.0	$\sim Ba_2Ca_{0.5}(Al_5Si_{11}O_{32})\ 12H_2O$
chabazite [16]	2.49	1.52	2.48	>1.5	>1.25	7.0	2.0	$(Ca,Sr)_{1.7}(Al_{3.7}Si_{8.3}O_{24})\ 13H_2O$
stilbite [17]	3.0	≤0.8	≥3.2	?≥2.8*	?0	6.9	1.77	$Na_{1.28}Ca_{4.18}Mg_{0.18}(Al_{10.3}Si_{25.7}O_{72})\ 34.07H_2O$
epistilbite [18]	3.63	0.0	4.0	2.5*	0	9	1.56	$Ca_{2.59}Na_{1.06}K_{0.1}(Al_{6.29}Si_{17.71}O_{48})\ 15.74H_2O$
brewsterite [19]	4	0	4	2.5	0	10	2.0	$Ba_{0.5}Sr_{1.5}(Al_4Si_{12}O_{32})\ 10H_2O$

a mean coordination number of cavity cations (C)
b mean valence electron number of C atoms
N neutron refined
* with water molecules bound to 2 or ?more C atoms

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Table 2 gives values for the mean numbers, per Al atom, of O atoms with specified coordinations (so-called *identifiers for the coordination of O atoms*) calculated from the refinements of structures of natural zeolites. All zeolite structures with a low water content and whose chemical composition corresponds to the theoretical formula were examined. However, for zeolites with a high water content, structures were considered, provided that disorder and partial occupation on the cavity cation and water oxygen sites were not too great. For these structures, the cavity cations polyhedra were determined with interatomic distance calculations; O polyhedra with (O-O) distances greater than about 2.6 Å were considered.

As a supplement, table 3 gives a review of natural zeolites as classified by Gottardi and Galli (1985), with parameters, which, for some of them, may easily be calculated from the ideal chemical formula, and may also be used as an indication for possible coordinations of the chemical constituents within the structures.

For the examined structures of table 2, the O coordinations given previously in terms of a model (see table 4, left column) are indeed observed in zeolite structures, except for the water oxygen coordination. In practice, it is frequent that some water oxygens are found coordinated to one, two or maybe even three cavity cations (shown with a star under r in table 2). This appears in particular in zeolites with cavity cations of valence one. In these structures, the positive charge excess of the water oxygens as well as the total valence deficiency around the Al-centered O tetrahedra are consequently increased (compare fig. 2 in Engel, 1989, field for $e_C = 1$). For these structures also, the equations for the identifiers for the coordination of the O atoms given in the preceding papers should be used with restriction. For all examined structures, the observed values for the mean (C-O) bond strength calculated over each structure ($e_C/<CN_C>$; max. observed value: 0.3333 v.u. for wairakite; min. observed value: 0.132 for clinoptilolite; table 3) are in agreement with values found by the theory ($0.40 \leq e_C/<CN_C> \leq 0.125$; fig. 4 in Engel, 1989).

For the mean composition of the O atoms forming the Al-centered tetrahedra, the number of O atoms which are deficient in positive valences (see column $(g + i')$ in table 2) are found on average to be more than two. Bikitaïte, whose cavity cations (Li atoms) are coordinated to 4 oxygens or water oxygen, is the only known exception to this condition (see a comment in Engel, 1989). Further, the condition for the parameter $V (1/2 \leq V \leq 1)$ is generally fulfilled for all examined zeolite structures. The following definition for V is applied: V = number of C-coordinated water oxygens per number of valence deficient O atom (compare equ. (5) in Engel, 1988 $[V = r/(i' + g)]$). Two known exceptions are natrolite ($V = 1/3$) and analcime ($V = 1/4$) in which structures water oxygens are coordinated to 2 cavity cations (see also next paragraph). Finally, the condition given as $1 \leq r \leq 4$, rewritten as $1 \leq w/x \leq 4$ in the right columns of table 1, is verified for all zeolites (table 3).

In the structures of natrolite, edingtonite and scolecite, which were refined from neutron diffraction data (table 2), the H atoms are observed to be coordinated to two

TABLE 3.

General review for natural zeolites: ideal chemical formula and classification after Gottardi and Galli, framework density, "structural" and chemical parameters.

#	(%)	mineral [ref.]	framework density k^1 (T/1000Å³)		w/x	$<CN_C>^2$	$<e_C>^3$	$<CN_O>^4$	classification	
	$\dfrac{y}{(y+w+x/<e_C>)}$									

Zeolites with a low water content

#	(%)	mineral [ref.]	fw density	k	w/x	$<CN_C>$	$<e_C>$	$<CN_O>$	classification	formula
1.	34.0	gonnardite [2]	17.3	0.21	1.3	8.0	1.2	3.68	fibrous	$Na_{6.5}Ca_{1.5}(Al_{9.5}Si_{10.5}O_{40})\ 12.4H_2O$
2.	35.7	thomsonite	17.7	0	1.2	8.0	1.67	3.38	fibrous	$Na_4Ca_8(Al_{20}Si_{20}O_{80})\ 24H_2O$
3.	37.5	paranatrolite	16.7	1	1.5		1.0		fibrous	$Na_{16}(Al_{16}Si_{24}O_{80})\ 24H_2O$
4.	37.5	edingtonite	16.7	1	2	10.0	2.0	3.29	fibrous	$Ba_2(Al_4Si_6O_{20})\ 8H_2O$
5.	42.9	natrolite	17.8	1	1	6.0	1.0	3.33	fibrous	$Na_{16}(Al_{16}Si_{24}O_{80})\ 16H_2O$
6.	42.9	tetranatrolite [25]	17.6	1	1	6.0	1.0	3.33	fibrous	$Na_{16}(Al_{16}Si_{24}O_{80})\ 16H_2O$
7.	42.9	mesolite	17.6	1	1.33	6.5	1.5	3.11	fibrous	$Na_{16}Ca_{16}(Al_{48}Si_{72}O_{240})\ 64H_2O$
8.	42.9	scolecite	17.4	1	1.5	7.0	2.0	3.0	fibrous	$Ca_8(Al_{16}Si_{24}O_{80})\ 24H_2O$
9.	44.4	laumontite	17.1	2	2	?<8.0	2.0	?<3.0	s.c. 4-rings	$Ca_4(Al_8Si_{16}O_{48})\ 16H_2O$
10.	47.1	leonhardite	17.6	2	1.75	??7.75	2.0	?2.95	s.c. 4-rings	$Ca_4(Al_8Si_{16}O_{48})\ 14H_2O$
11.	50.0	analcime[h]	18.5	2	1	6.0	1.0	2.86[h]	s.c. 4-rings	$Na_{16}(Al_{16}Si_{32}O_{96})\ 16H_2O$
12.	50.0	bikitaite	20.3	2	1	4.0	1.0	2.86	Mordenite	$Li_2(Al_2Si_4O_{12})\ 2H_2O$
13.	54.5	yugawaralite	18.3	4	2	8.0	2.0	2.8	s.c. 4-rings	$Ca_2(Al_4Si_{12}O_{32})\ 8H_2O$
14.	57.1	wairakite	18.9	2	1	6.0	2.0	2.71	s.c. 4-rings	$Ca_8(Al_{16}Si_{32}O_{96})\ 16H_2O$

Zeolites with doubly connected 4-rings chains

#	(%)	mineral [ref.]	fw density	k	w/x	$<CN_C>$	$<e_C>$	$<CN_O>$	classification	formula
15.	28.6	gismondite	15.3	0	2	6.5	2.0	3.21		$Ca(Al_2Si_2O_8)\ 4H_2O$
16.	30.8	amicite	15.2	0	1.25	6.75	1.0	3.76		$Na_4K_4(Al_8Si_8O_{32})\ 10H_2O$
17.	37.7	garronite	16.0	1.33	2.17		1.71			$NaCa_{2.5}(Al_6Si_{10}O_{32})\ 13H_2O$
18.	39.7	phillipsite [15]	15.8	1.82	2.18	9.74	1.4	3.41		$K_2\,Ca_{1.5}Na_{0.4}(Al_{5.5}Si_{10.5}O_{32})\ 12H_2O$
19.	40.7	gobbinsite	15.9	2.4	2.2		1.0			$Na_5(Al_5Si_{11}O_{32})\ 11H_2O$
20.	42.7	merlinoite	16.0	3.11	2.67		1.3			$(K,Na)_5(Ba,Ca)_2(Al_9Si_{23}O_{64})\ 24H_2O$
21.	42.9	mazzite	16.1	3.2	2.8		1.5			$K_3Ca_{1.5}Mg_2(Al_{10}Si_{26}O_{72})\ 28H_2O$
22.	43.1	harmotome [15]	16.1	2.4	2.4	9.85	2.0	3.11		$Ba_2\,Ca_{0.5}(Al_5Si_{11}O_{32})\ 12H_2O$

Other zeolites with a high water content

#	(%)	mineral [ref.]	fw density	k	w/x	$<CN_C>$	$<e_C>$	$<CN_O>$	classification	formula
23.	30.0	willhendersonite	15.0	0	1.67		1.5		6-rings	$K_2Ca_2(Al_6Si_6O_{24})\ 10H_2O$
24.	32.4	faujasite	12.9	2.4	3.92		1.5		6-rings	$Na_{20}Ca_{12}Mg_8(Al_{60}Si_{132}O_{384})\ 235H_2O$
25.	34.8	gmelinite [20]	14.6	2	2.75	≈7.5	1.0	≈3.49	6-rings	$Na_8(Al_8Si_{16}O_{48})\ 22H_2O$
26.	35.8	levyne	15.3	2	3.0	6.22	1.71	3.07	6-rings	$NaCa_{2.5}(Al_6Si_{12}O_{36})\ 18H_2O$
27.	36.1	chabazite [16]	14.5	2.49	3.51	≈7.0	2.0	≈3.05	6-rings	$(Ca,Sr)_{1.7}(Al_{3.7}Si_{8.3}O_{24})\ 13H_2O$
28.	41.9	offretite	15.5	3.2	3.0		1.67		6-rings	$KCaMg(Al_5Si_{13}O_{36})\ 15H_2O$
29.	43.5	stilbite	16.3	4	3.33	6.9	1.8	2.93	Heulandite	$NaCa_4(Al_9Si_{27}O_{72})\ 30H_2O$
30.	45.2	barrerite	16.3	5	3.25		1.0		Heulandite	$Na_8(Al_8Si_{28}O_{72})\ 26H_2O$
31.	45.4	erionite [21]	16.0	5	3.5	?10.5	1.4	?3.16	6-rings	$NaK_2MgCa_{1.5}(Al_8Si_{28}O_{72})\ 28H_2O$
32.	46.7	stellerite [22]	16.3	5	3.5	9.0	2.0	2.92	Heulandite	$Ca_4(Al_8Si_{28}O_{72})\ 28H_2O$
33.	48.2	heulandite [23]	17.1	4	2.67	7.1	1.8	2.87	Heulandite	$(Na,K)Ca_4(Al_9Si_{27}O_{72})\ 24H_2O$
34.	48.6	epistilbite	17.6	4	2.67	9.0	2.0	2.92	Mordenite	$Ca_3(Al_6Si_{18}O_{48})\ 16H_2O$
35.	50.0	brewsterite	17.5	4	2.5	10.0	2.0	2.95	Heulandite	$Sr_2(Al_4Si_{12}O_{32})\ 10H_2O$
36.	53.6	clinoptilolite [24]	17.2	8	3.33	7.6	1.0	2.93	Heulandite	$(Na,K)_6(Al_6Si_{30}O_{72})\ 20H_2O$
37.	54.0	mordenite	17.2	8	3.5		1.33		Mordenite	$Na_3KCa_2(Al_8Si_{40}O_{96})\ 28H_2O$
38.	55.7	dachiardite	17.5	8	3.14		1.2		Mordenite	$(Na,K,Ca_{0.5})_4(Al_4Si_{20}O_{48})\ 12.56H_2O$
39.	56.1	ferrierite	17.7	8	3.33		1.71		Mordenite	$(Na,K)Mg_2Ca_{0.5}(Al_6Si_{30}O_{72})\ 20H_2O$

[1] $k = 2(y/x-1)$ (equ.(1) in Engel, 1988).
[2] mean coordination number of C atoms calculated from structure refinements.
[3] mean valence electron number per C atom.
[4] mean O coordination number; equ. (1).
[h] no H bonds in the structure ($CN_H = 1$)

O atoms: one water O ("donor") and one O "acceptor" which is found among the O coordinated to two heavy cations (O surrounded by (Si Al) — identifier g — or (Si Si) — identifier k). For analcime, a structure which is also obtained from neutron data, the H atoms are bound only to the water oxygens (the shortest (possible O "acceptor"-H atom) distance is 2.53 Å compared to a max. distance of 2.4 Å for a possible H bond given in Baur, 1972); the H coordination number should then be equal to one, which deviates from the scheme for the H coordination given in Engel (1989). Thus, a proper analysis for H bonds should be based not only on the positive valence deficiencies of O atoms.

3. RELATION BETWEEN THE Si CONTENT
AND THE WATER CONTENT
DEDUCED FROM THE O COORDINATION NUMBERS

In Engel (1986), the significance of the O coordination numbers was discussed. The *mean coordination number of oxygen atoms* ($<CN_O>$) in a structure was shown to be relevant of the numbers of the O atoms coordinated to 2, 3 or 4 or more cations, in that the coordination number of most O atoms in a crystal structure is the number which is the closest to $<CN_O>$ (Engel, 1986). In structures of Ca-bearing zeolites, the O atoms were observed to be surrounded by 2, 3 or 4 cations, most of

TABLE 4.

Model for the O coordinations and occurrence in zeolite structures with cavity cation (C)
of valence one [$e_C = 1$] or two [$e_C = 2$] (identifiers for the coordination of O atoms in square parentheses).

Cations coordinated to central O atoms		occurrence in structures with $<e_C>/<CN_C>$ (range)	estimated sum of bond valences (without H bonds) (v.u.)	'function' of O atoms (Engel, 1989)	O coordination number without H bonds
(Si Si)	[k]		2.0	possible acceptor	2
(Si Al C C)	[l]	0.125 - 0.167	≥2.0	'overloaded'	4
(Si Al C)	[i']	0.125 - <0.25	<2.0	possible acceptor[1]	3
	[i"]	0.25 - 0.333	≥2.0	'overloaded'	3
(Si Al)	[g]	≈0.14[2]- 0.333	1.75	acceptor[1]	2
(C H H)	[r]		≈2.0	donor - ?acceptor[3]	3
(H H)	[s]		≈2.0	donor - ?acceptor[3]	2

[1] whose sum of the cationic bond strength is below 2.0 v.u.; therefore also called "valence deficient"
[2] occurrence in structures containing cavity cations of valence one with water O bound to 2 cavity cations (see text)
[3] the sum of bond valences may be inferior to 2.0 v.u. if a correction relative to the bond length distortion is applied to the (H-O donor) bonds

them being coordinated to 3 cations (Engel, 1986), the mean O coordination number being close to 3.0. This corresponds to the model for the O coordination (table 4).

The mean O coordination number, calculated over the chemical formula, is equal to the sum of the coordination numbers of the cations times stoechiometric composition divided by the number of oxygen atoms in the formula; for the theoretical composition of zeolites (see above formula):

$$<CN_O> = \frac{x<CN_C>/<e_C> + 4(x+y) + 2(2w)}{2(x+y) + w} \tag{1}$$

In this expression, the H atoms are supposed to be coordinated to 2 O atoms, one "donor" and one "acceptor".

The *mean numbers, per Al atom, of O atoms with given coordination numbers (N_2, N_3 and N_4)* are calculated in the appendix with the *assumption* that, for zeolites, all O atoms are *surrounded by maximum 4 cations (H bonds included)*. The H atoms are there supposed to be "accepted" either by the less coordinated O atoms (identifiers *g, k* and *s* in table 4) or by the cationic valence deficient O atoms (identifiers *g* and *i'*) or by water oxygens themselves (*s* and even *r*) (see appendix).

There follows that if N_2 O atoms, calculated on average per Al atom, are coordinated to 2 cations only,

$$N_2 = k - (k_H + k_{HH}) \tag{2}$$

$(k_H + k_{HH})$: mean number, per Al atom, of O atoms coordinated to two Si atoms and one or two H atoms $[0 \le (k^H + k^{HH}) \le k]$. For the average number, per Al atom, of the O atoms coordinated to 3 cations (N_3):

$$N_3 = 8 - <CN_C>/<e_C> + 2(k_H + k_{HH}) \tag{3}$$

$<CN_C>/<e_C>$: mean number of (C-O) bonds [C = cavity cation] per Al atom; the inverse, $<e_C>/<CN_C>$: mean bond strength of the cavity cation — O atom bond, see appendix A in Engel (1988).

Subtracting equations (2) and (3) from the total number of O atoms contained in a structure (= $2(x+y) + w$, see the theoretical chemical formula), we find for the average number, per Al atom, of the O atoms surrounded by 4 cations:

$$N_4 = <CN_C>/<e_C> - 4 + w/x - (k_H + k_{HH}) \tag{4}$$

For the mean coordination number of O atoms, we may now write:

$$<CN_O> = (2N_2 + 3N_3 + 4N_4) / (N_2 + N_3 + N_4) \tag{5}$$

As calculated in the appendix, this expression is, for the parameters shown in table 3, equal to:

$$\langle CN_O \rangle = \frac{\langle CN_C \rangle / \langle e_C \rangle + 2w/x}{k + 4 + w/x} + 2 \tag{6}$$

Developping this expression and using equ. (1) in Engel (1988) $[k = 2(y/x - 1)]$, one obtains expression (1).

For $\langle CN_O \rangle = 3.0$, equation (6) becomes:

$$w/x = k + 4 - \langle CN_C \rangle / \langle e_C \rangle \tag{7}$$

or
$$w/x = 2y/x - \langle CN_C \rangle / \langle e_C \rangle + 2 \tag{7'}$$

For zeolites with *a high water content,* the mean O coordination number tends to be close to 3.0 (table 3). According to equ. (7), the highest Si content relative to maximal water content and $\langle CN_C \rangle / \langle e_C \rangle$ (w/x = 4 in table 1; $(\langle e_C \rangle / \langle CN_C \rangle)_{min} = 0.125$ equ. (11) in Engel, 1988) corresponds then to k = 8 or y/x = 5.

The maximal values for w/x and y/x observed for highly hydrated Si-rich zeolites (table 3) are for mordenite [$Na_3KCa_2(Al_8Si_{40}O_{96})$ 28 H_2O] with w/x = 3.5 and y/x = 5; for the maximal observed value of $\langle CN_C \rangle / e_C$ [$\langle CN_C \rangle / e_C = 7.6$ for clinoptilolite, $(Na, K)_6(Al_6Si_{30}O_{72})$ 20 H_2O)], w/x = 3.33 and y/x = 5 ($\langle CN_O \rangle = 2.93$).

Now, for zeolite structures whose mean O coordination number is equal to 3.0, according to equation (5),

$$N_2 = N_4$$

Furthermore, the number of the O atoms surrounded by 2 cations as well as those surrounded by 4 cations should not exceed the number of the O atoms coordinated to 3 cations (see above). Thus

$$N_2 \leq N_3 \qquad \text{and} \qquad \text{as } N_2 = N_4: \quad N_3 \geq (N_2 + N_3 + N_4) / 3$$

We shall use these relations in order to establish a limit between the *Si-rich and the Al-rich zeolites* characterized by a *high water content.* The value for N_2 ($= k - (k_H + k_{HH})$) should not exceed one third of the amount of all O atoms in a structure. Thus if $k \geq (N_2 + N_3 + N_4) / 3$ (see examples in table 3), some of these O atoms are expected to be obligatory bound to H atoms (this amount is quantified with k_H^{min}) and:

$$k_H^{min} = k - (N_2 + N_3 + N_4) / 3$$
$$= k - (w/x + k + 4) / 3$$

If $k_H^{min} = 0$ then:

$$w/x = 2k - 4 \qquad (8)$$

This expression is valid for $2.0 \leq w/x \leq 4.0$; consequently $3.0 \leq k \leq 4.0$. Furthermore, for this limit, $k = 8 - <CN_C>/<e_C>$. Thus, for the Si-rich zeolites, $w/x \leq 2k - 4$. In their structures, not all O atoms coordinated to 2 Si atoms are expected to be "acceptor" of H atoms. Therefore $<CN_O> \leq 3.0$ and according to (7):

$$k \geq w/x + <CN_C>/<e_C> - 4 \qquad (9)$$

Both conditions (8) and (9) are fulfilled for stilbite (table 3), whereas for erionite ($k = 5$), whose cavity cation is given with a high coordination in table 3, equation (8) is not verified nor for offretite, for which a high mean coordination of cavity cations might also be expected.

For zeolites *with a low water content,* a limit between *Si-* and *Al-rich structures* may be drawn with:

$$k + g = 2 w/x ,$$

provided that, as before, some O atoms are bound to 2 Si atoms only. Using the equation for the identifier g ($g = 4 - <CN_C>/<e_C> + r$, table 2 in Engel, 1988), since $w/x = r$, one obtains expression (9). If $<CN_C>/<e_C> = 4$ in this expression (see laumontite in table 3) then

$$k = w/x \qquad (10)$$

for $1.0 \leq w/x \leq 2.0$ and $1.0 \leq k \leq 2.0$.

Thus, an oxygen mean coordination number equal to 3.0 ($<CN_O> = 3.0$) seems relevant for a distinction between *Al-rich* and *Si-rich zeolites.*

4. LIMITS FOR THE GROUPS OF THE CLASSIFICATION

In the ternary representation of fig. 2, natural zeolites are shown as a function of the water content (w/x), of the Si content expressed with k and of the mean number of (O-cavity cation) bonds per Al atom ($<CN_C>/<e_C>$). The specific signs are
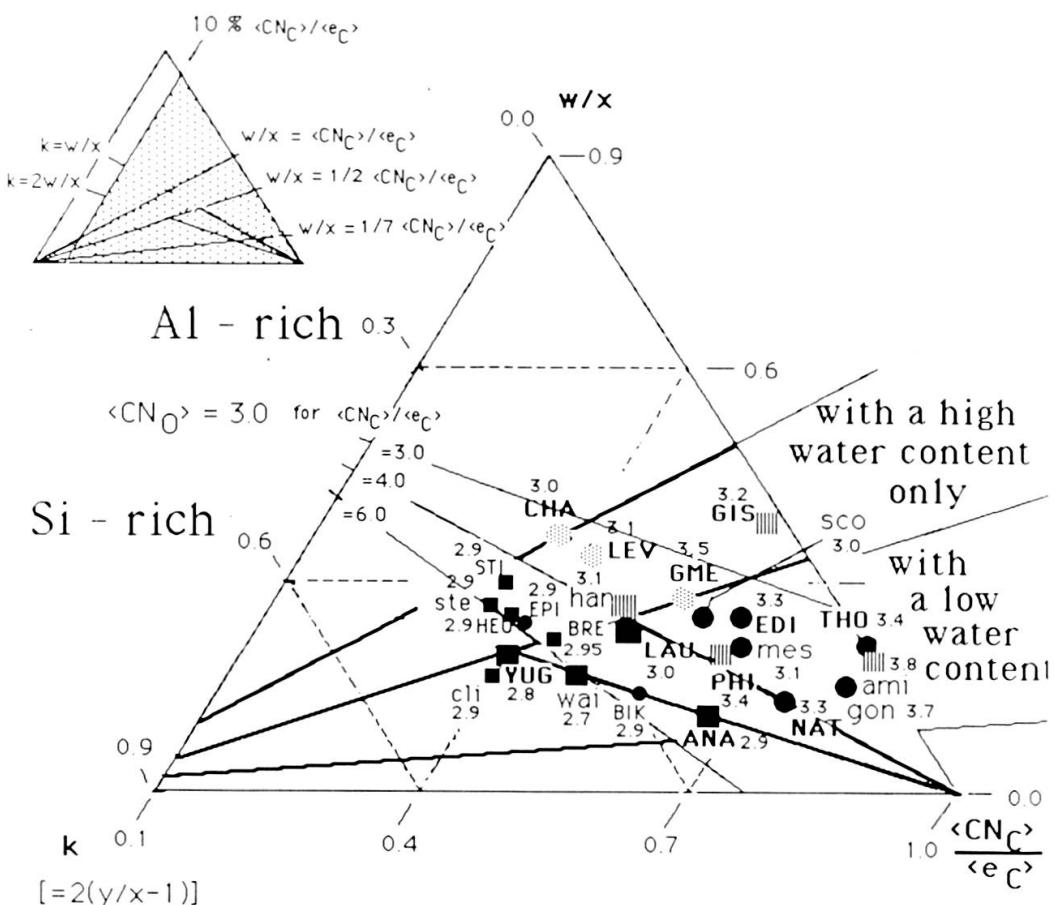
FIG. 2.

Natural zeolites plotted as a function of the mean number of (cavity cation - O) bonds per Al atom ($<CN_C>/<e_C>$), the mean number, per Al atom, of O atoms bound to 2 Si atoms (identifier k) and the water content relative to the Al content (w/x). Small triangle: limits as discussed in text. Other lines are for the mean O coordination number of 3.0 cations ($<CN_O> = 3.0$) with the specified values for $<CN_C>/<e_C>$ (equ. 7). Codes are according to the recommendations of the IZA.

for the groups of the classification according to Gottardi and Galli (1985) (compare also the values given in table 2). The mean O coordination number ($<CN_O>$) is shown with straight lines for the ideal value of mean 3.0 cations per O atom and the specified values of $<CN_C>/<e_C>$ (equ. (7)). The numbers near codes give for each examined structure the calculated value of $<CN_O>$ (compare table 3). In structures with a relative high value for $<CN_C>/<e_C>$, the oxygen mean coordination number is also high (max. values: amicite 3.8; gonnardite 3.7; both calculated for $CN_H = 2$). Finally, for the zeolite structures with a high water content, the mean O coordination number for O atoms tends to be close to 3.0.

From the limitation for water molecules according to the Al and cavity cation coordination (second column of table 1), one retains the limit between zeolites with *a high water content* and those with *a low water content* given as:

$$w/x = 1/2 \; <CN_C>/<e_C>$$

From fig. 2, one finds that structures situated above this limit, belong to the Mordenite and Heulandite groups as well as to the 6-ring zeolites. The zeolites with doubly connected 4-ring chains are found on both sides of this limitation (see also next section).

A limit between *Al-rich zeolites* and *Si-rich zeolites,* drawn with $<CN_O> = 3.0$, seems relevant for a limitation between zeolites with 6-rings, with doubly connected 4-rings or the fibrous zeolites *and* the ones of the Heulandite or the Mordenite groups plus those with singly connected 4-rings (see values in table 3). For zeolites with a low water content, equation (10) corresponds well to this limit.

In fig. 2, the *maximal and minimal conditions for natural zeolites* are given with $<CN_C>/<e_C> = w/x$ and with the function $<CN_C>/<e_C> = 7\,w/x$ (table 1) respectively. On the other side, the lowest water content compared to the Si content for zeolites with a low water content is equal to 1/2 (i.e. wairakite with k = 2 for $<CN_C>/e_C = 3$ and $(w/x)_{min} = 1$, table 3; for the ideal formula of this mineral $N_4 = 0$ and $<CN_O> = 2.71$ for $CN_H = 2$).
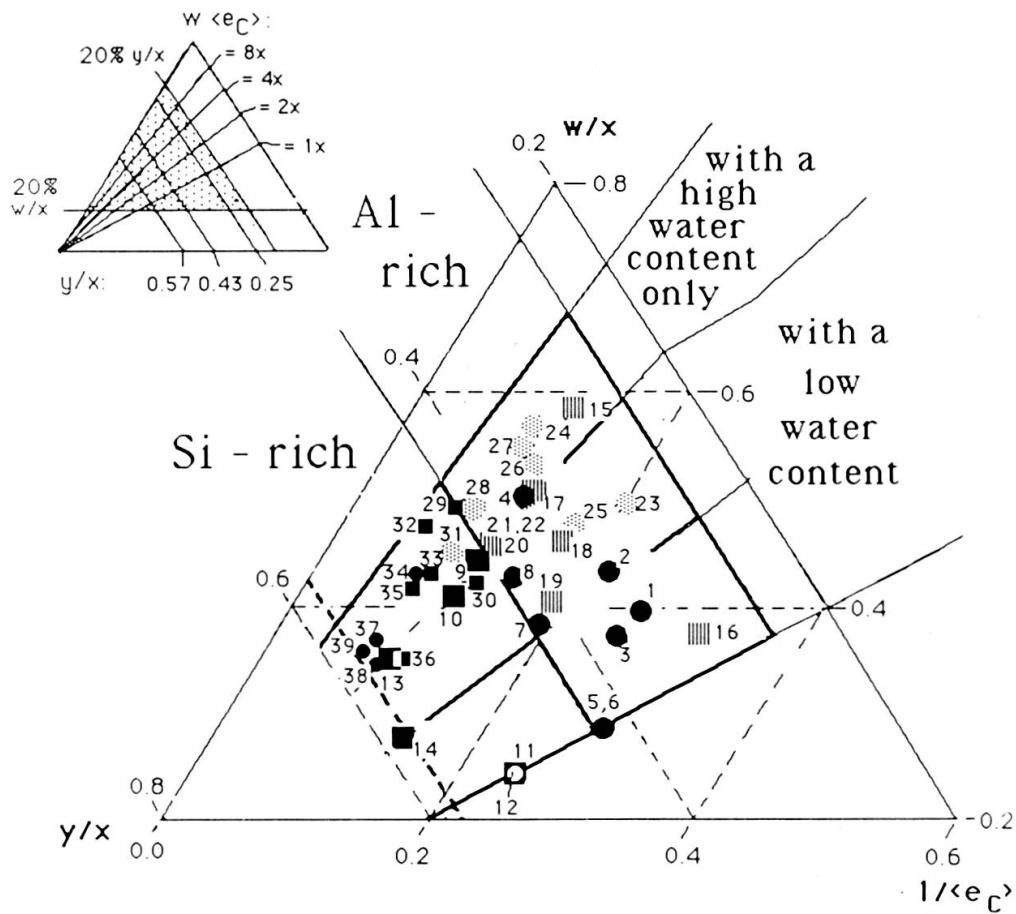

Fig. 3.

Natural zeolites shown as a function of the stoechiometric compositions of Si atoms (y), water molecules (w) and cavity cations $(x/<e_C>)$, all relative to the Al composition (x). Small triangle: limits as discussed in text (table 1 and fig. 1). Numbers refer to natural zeolites as cited in table 3.
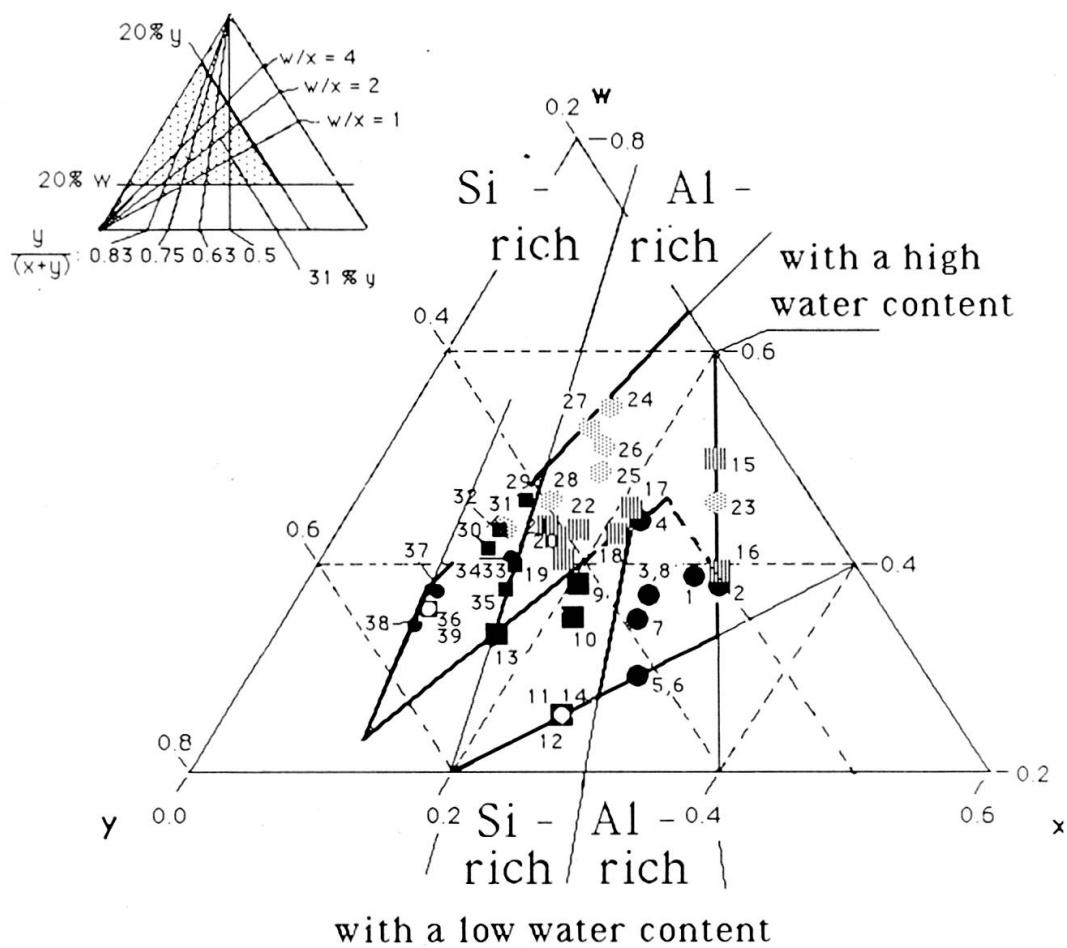
FIG. 4.

Natural zeolites shown as a function of the Si, water and Al compositions.
Small triangle: limits as discussed in text or from table 1.
Numbers refer to natural zeolites as cited in table 3.

In fig. 2, 3 and 4, the signs are for the groups of the classification by *Gottardi and Galli*
(legend in table 5).
Values are calculated from the chemical formula given in table 3.

Up to now, we have analysed the possible composition for zeolites in terms of
the cavity cation mean coordinations as well as of Si and water content relative to the
Al content. Other limits for the groups of zeolites according to the classification in
terms of Al or cavity cation stoechiometric compositions are observed in the
ternary diagrams of fig. 3 and 4. One limit is given by the ratio
$y / (y + w + 1 / <e_C>) \approx 0.43$ (fig. 3 and 1) which defines the *Si-rich* from the *Al-
rich zeolites*. A range for this value is calculated for zeolites with *a low water content*,
when one inserts equ. (10) into the above ratio: 0.43 is obtained for $y/x = 1.5$ and
$<e_C> = 1.0$ and 0.44 for $y/x = 2.0$ and $<e_C> = 2.0$. However, for zeolites with
a high water content (thus using equ. (8)), one obtains a wider range for this value
(0.375-0.50). In fig. 4, the same limits are calculated for the ratio $y/(x + y)$; for
zeolites with *a low water content*, $0.60 \leq y/(y + x) \leq 0.667$, whereas for zeolites with

a high water content, $0.71 \leq y/(y+x) \leq 0.76$. In this figure, an other chemical limit may be observed between zeolites *with doubly connected 4-rings* and those *with 6-rings* as a function of the water content expressed with w/x; the zeolites of the first group are generally less hydrated than the ones of the second group. This limit is however not valid for willhendersonite *(6-rings).* For this mineral as well as for amicite *(doubly connected 4-rings),* values for w/x are below 2.0; these minerals are also remarkably Si-poor with values for $y/(y+w+x/<e_C>)$ below 33% (fig. 3). This is in fact the minimal calculated value for zeolites with *a low water content* for $(y/x)_{min} = 1$ and $(w/x)_{min} = 1$ for $(1/e_C)_{max} = 1$ (see fig. 1 and 3). The same limitation calculated in fig. 4 in terms of $y/(y+x+w)$ for $[y/(y+x)]_{min} = 0.5$ is less significant. The minimal value for $y/(y+w+x/<e_C>)$ calculated for zeolite with *a high water content* is theoretically equal to 25% $[(y/x)_{min} = 1$ and $(w/x)_{min} = 2$ for $(1/e_C) = 1]$; $y/(y+w+x/<e_C>)$ is for gismondine equal to 28.6% (ideal formula, table 3). The maximal observed value of $y/(y+w+x/<e_C>)$ is for wairakite (57.1%, ideal formula; fig. 1 and 3).

5. A GLOBAL REVIEW FOR ZEOLITES ACCORDING TO THE GROUPS OF THE CLASSIFICATION

Zeolites may be classified according to their stoechiometric composition, by the Al respectively Si, and water contents (table 5). Any attempt to classify zeolites according to the stoechiometric composition of cavity cations would bring incomplete results (i.e. fig. 3) given that the coordination of these cations is important for these structures. The following global description of the groups of the classifica-

TABLE 5.

"Structural" and chemical compositions for natural zeolites with ideal composition $C_{x/<e_C>}(Al_xSi_yO_{(x+y)2})$ *w* H_2O *(C: cavity cation of valence one or two). Limits for the groups of the classification.* $y\% = y/(y+w+x/<e_C>) \times 100$. *Other letters: identifiers for the coordination of O atoms (see table 4). Exceptions to the drawn limits (see text) are shown with small characters.*
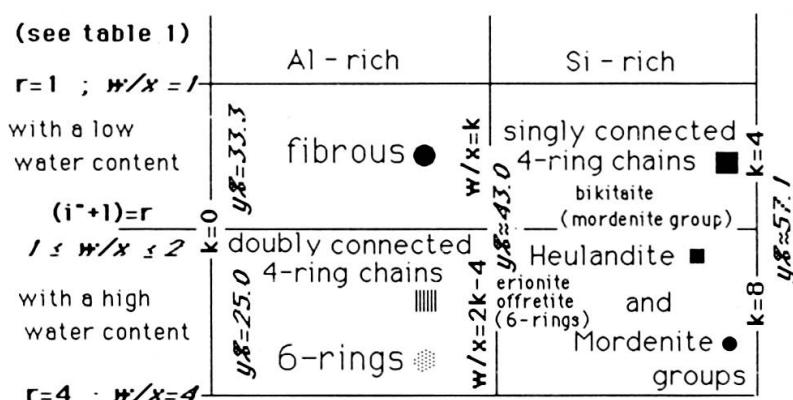
tion for natural zeolites of Gottardi and Galli (1985) takes account of the coordinations of the O atoms, which are related to the cavity cation coordinations, to the Si and to the water contents relative to the Al content (fig. 2). As shown in fig. 1, framework density compared to the relative Si content is also characteristic of the groups of the classification.

Zeolites with a low water content

For these minerals, the water content does not exceed the limit shown in relation to the mean composition of the cavity cation polyhedra given in table 1. The framework density (FD) is high; it is higher than a limitation given in fig. 1, which is estimated to FD $\approx$ 12.7 + 10 y/(y + w + x/ $<e_C>$).

Zeolites with singly connected 4-ring chains are Si-rich. In the structure, the content of water molecules is inferior to the number of the O atoms linked to 2 Si atoms (see equ. (10)). They are therefore characterized by a high framework density (above 17.2 T/1000 Å^3) and a low O mean coordination number ($<CN_O>$ < 3.0). For the Al-rich zeolites, the *fibrous zeolites,* the low Si content is characteristic of a lower framework density (above 16.5 T/1000 Å^3) and a relative high mean O coordination number (above 3.0). One notices, that these minerals often contain cavity cations of valence one.

Zeolites with doubly connected 4-ring chains

Zeolites belonging to this group are Al-rich. Generally, more than 2 water molecules are found per Al atom within the structure. Although the ratio w/x is relatively low, for the examined structures (table 2), 3 or more O atoms forming the Al-centered tetrahedra are valence deficient (column *(g + i′)* in table 2). This may be due to a relative low value for $<CN_C>$/$<e_C>$ or to a high coordination (CN_C > 8) for some of the cavity cations (i.e. K in phillipsite, Ba in harmotome). As a consequence, the structures of this group should correspond to the condition for *a high water content* ((i″ + 1) $\leq$ r; table 1) (see in table 2: amicite, gismondine, phillipsite, harmotome). As for other Al-rich zeolites with a high water content (with *6 rings*), the mean O coordination number is above 3.0 and the value for the framework density is below 16.3 T/1000 Å^3.

Other zeolites with a high water content

The zeolites with relative low coordination number (below 3.0 cations on average per O atom) are also those with a high Si content. These minerals crystallize generally with a relatively small "free" volume, which is estimated with a framework density of above 16.3 T/1000 å^3 (fig. 1). These are zeolites of the *Heulandite group* and the *Mordenite group.*

Zeolites with 6-rings are also characterized by a high water content and are Al-rich. Their frameworks present spacious cages and show the lowest framework density relative to the Si content for zeolites (fig. 1). Some of the water molecules are unbound to cavity cations and for the two examined structures (chabazite, levyne), the number of O "acceptors" (valence deficient) per Al-centered tetrahedron is below 3.

6. CONCLUDING REMARKS

From the theoretical chemical formula of zeolites and the known coordinations of the cations in their structures, we postulated a model for the O coordinations. With this model, we deduced from the existing crystallochemical rules the possible relationship which may exist between the number of oxygen atoms with defined coordination spheres.

The examination of about 20 structures of natural zeolites showed that the model first established is generally fulfilled, except for the coordinations of the water molecules with cavity cations. Our work on real structures was however considerably hindered by incomplete reports of several structures, especially those with a high water content, in regard to the cavity cations and their coordination polyhedra.

This global analysis of zeolite structures is exclusively based on averaged numbers calculated over each structure. It shows how chemical composition and "structural" composition, a composition based on the atom coordinations in structures, are interrelated. Limiting compositions for natural zeolites are defined. Several conditions expressed with simple equations are shown to be significative for the groups of the classification for natural zeolites (Gottardi and Galli, 1985), which follows the topology of the O tetrahedra in structures, as usually done for silicates. If chemical limits may be deduced from the observations only, "structural" limits were derived from crystallochemical rules according to a certain logic of the structures. The general considerations thus established in this analysis may help in a better understanding of zeolites. In turn, better discussions of the results of structure refinements, especially in regard to the cavity cation coordination, may help in completing this numerical analysis of zeolites structures, in particular for the zeolites with a high water content. Finally, more structure refinements carried out with neutron diffraction may complete the understanding of the function of the hydrogen atoms in zeolite structures.

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APPENDIX

THE CALCULATION OF THE NUMBERS OF O ATOMS COORDINATED TO 3 OR 4 CATIONS

This calculation is carried out with the following assumptions:

1° All H atoms are bound to two O atoms and the O "acceptors" of H atoms may be the k, i', g, r or s O atoms.

2° None of the O atoms may be bound to more than 4 cations (H bonds included).

3° The s and g O atoms, as they may be strongly deficient in cationic valences, are supposed to be always "acceptors".

First, let us calculate expressions (2) and (3) of Engel (1988) in order to eliminate l:

$$l + g + i = 4 \tag{2}$$

$$\alpha r + i + 2l = <CN_C>/<e_C> \tag{3}$$

α: mean number of cavity cations bound to the r C-coordinated water oxygens; $1 \leq \alpha \leq 2$.

Thus: $$-i - 2g + \alpha r = <CN_C>/<e_C> - 8 \tag{A1}$$

The total number of O bound to 3 cations are:

$$N_3 = r_C + i - i'_H + k_H + s_H + g_H \tag{A2}$$

The index H is for the O atoms "acceptors" to one H atom; r_C: number, per Al atom, of water oxygens bound to one C atom only. As all H atoms are bound to 1 O "acceptor":

$$2w/x = 2(s_{HH} + g_{HH} + k_{HH}) + s_H + g_H + i'_H + r_H + k_H$$

The index HH is for the O atoms "acceptors" to two H atoms. With equ. (4) in Engel (1988) $[r + s = w/x]$; further since $r = r_C + r_{CC} + r_H$ (r_{CC}: number, per Al atom, of water oxygens bound to two C atoms); and finally with assumption 3° ($s = s_H + s_{HH}$ and $g = g_H + g_{HH}$), this expression becomes:

$$r + r_C + r_{CC} = s_{HH} - s + g_{HH} + g + i'_H + k_H + 2k_{HH} \tag{A3}$$

The expressions (A3) and (A1) are inserted into (A2) in order to eliminate the s, g and i parameters. As a consequence:

$$N_3 = 8 - <CN_C>/<e_C> + 2(k_H + k_{HH}) + (\alpha - 1)r - r_{CC}$$

From the above definitions for α and r and assumptions, we may write:

$$\alpha = (2r_{CC} + r_C + r_H)/r \qquad \text{(r_H O atoms are bound to one C atom in plus of being "acceptor")}$$

Since $r_C + r_H = r - r_{CC}$: $r_{CC} = (\alpha - 1) r$

Thus $$N_3 = 8 - <CN_C>/<e_C> + 2(k_H + k_{HH})$$

The value for N_2 is equal to $k - (k_H + k_{HH})$

k: total number per Al of O atoms bound to at least 2 Si atoms

Since we assume that O atoms are coordinated to a maximum of 4 cations, the value for N_4 is calculated when substracting N_2 and N_3 from the total number of O atom per Al atom, which is $2(y/x + 1) + w/x$ (see theoretical chemical formula).

$$N_4 = 2(y/x + 1) + w/x - 8 + <CN_C>/<e_C> - k - (k_H + k_{HH})$$

Inserting the equation for k ($= 2(y/x - 1)$; equ. (1) in Engel, 1988):

$$N_4 = <CN_C>/<e_C> - 4 + w/x - (k_H + k_{HH})$$

The calculation of the *mean O coordination number* $<CN_O>$ is, for the numerator of equ. (5):

$$
\begin{aligned}
2N_2 + 3N_3 + 4N_4 &= 2(k - (k_H + k_{HH})) + 3(8 - <CN_C>/<e_C> + 2(k_H + k_{HH})) \\
&\quad + 4(<CN_C>/<e_C> - 4 + w/x - (k_H + k_{HH})) \\
&= <CN_C>/<e_C> + 8 + 4w/x + 2k
\end{aligned}
$$

For the denominator of equation (5):

$$N_2 + N_3 + N_4 = 2(y/x + 1) + w/x = k + 4 + w/x$$

Thus:

$$<CN_O> = \frac{<CN_C>/<e_C> + 2w/x}{k + 4 + w/x} + 2 \qquad \text{(compare equ. (6))}$$