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Crystallochemical Model and Prediction for Zeolite-Type Structures

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Abstract

A model for zeolite-type structures, which considers anion coordinations, is established on the basis of crystallochemical rules. Careful observation of 42 structures of zeolite-type minerals verifies the model. The numerical analysis which follows takes account of a scheme for charge transfer in the structures and allows structural chemical conditions to be established for these structures using simple numerical expressions. Accordingly, the atom coordinations in structures can be calculated directly from the chemical composition, which means that prediction of the atom coordinations in zeolite-type structures is now possible. In this paper, this prediction is carried out for some 30 known zeolite-type structures whose cavities, beside water oxygens or other anions, are filled with one type of cavity cation. The results are compared with the observations. It is shown that even the coordination of the cavity cation can be predicted within a fairly good approximation. For zeolite types with an interrupted framework, breaking of the tetrahedral framework is shown to be a consequence of charge equilibrium between the tetrahedral framework and the anions in cavities. A global structural analysis of zeolite-type structures has attracted greater interest as more and more synthetic or natural zeolite-type structures have become known. Refinements of several of these structures are, however, often incomplete because of disorder. At this stage of knowledge, the model and following numerical formulations may find several applications: *i.e.* in evaluating structures from chemical formulae, for the determination of possible order in disordered structures, for the synthesis of new materials, and for classification. This is a first attempt to define whole structures from chemical compositions using numerical expressions.

Introduction

Zeolite-type structures are characterized by a framework of O tetrahedra centered on cations of valences 2, 3, 4, or 5 valence units. Within the framework, cavities or channels are formed which enclose water molecules, hydroxides, various anions or anionic complexes, and other cations, the so-called cavity cations which are coordinated to oxygen atoms or other anions involved in shaping various polyhedra. Since for atoms in cavities, structure refinements often lead to important disorder, the description and classification of zeolite-type structures are based exclusively on geometric aspects of the framework. According to a topological system developed by Meier (1968), it is now possible to account for some 70 structure types of this class of mineral (Meier & Olson, 1987).

Groups of minerals having such a variety of structure and chemical composition, but which correspond to a precise structural definition, are not common in mineralogy. Zeolite-type structures offer in fact an appropriate field of work for structuralists who want to understand the relation between structural and chemical features. A numerical definition describing structural data was needed for database use, and this in turn, helped to establish limiting conditions for these structures in the form of numerical expressions.

For zeolites bearing exclusively Al and Si atoms in the O tetrahedra, cavity cations of charge $1+$ or $2+$ and water molecules in the channels or cages, a previous study has shown that structural features may be related to chemical composition by simple equations, if one considers a model established on the basis of the oxygen coordination spheres in these structures (Engel, 1988). The sum of bond strengths calculated around O atoms compared with the O charge revealed typical 'electrical' features within these structures (Engel, 1989*a*). Parameters were defined according to O coordinations, and the groups classifying natural zeolites established by Gottardi & Galli (1985) could be expressed by simple numerical expressions (Engel, 1989*b*). So, this analysis of structures according to oxygen coordinations gave an understanding of chemical composition which could even be related to tetrahedra topology.

A similar analysis is now extended to any zeolite-type structure. The analysis, which includes the previous considerations, is also based on crystallochemical rules and on a scheme for possible charge transfer in the structure. A model which considers anion coordination in structures is consequently estab-

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lished. From this point, simple numerical expressions are deduced, which permit calculation of the numbers of anions with specified coordinations directly from the chemical formula. The whole analysis is verified by observations on some 40 zeolite-type structures. In conclusion, mineral structures are presented whose composition differs from the definitions for a zeolite-type structure but which present the characteristics of a zeolite-type material following the criteria given in this paper.

This approach and the structural models given in this context may find applications in fields such as chemistry, for the synthesis of new materials or to predict possible cation or anion exchanges, in crystallography for calculating possible order in structures, and in physics for predicting the properties of these materials.

Zeolite types: definitions

A zeolite is defined as 'an aluminosilicate with a [tetrahedral] 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' (see Smith, 1984). Taking into account recent trends in structural work, Meier (1986) defines zeolite-type structures. Zeolite types may not necessarily show ion exchange nor reversible dehydration; however, they must show channels or cavities within an O tetrahedron framework. The term 'zeolite-like' is there used for analogous structures whose framework-O tetrahedra may be centered by Be, B, Al, Si, P, Ga, Ge as well as or instead of Si or Al atoms (all called *T* atoms in this paper), for structures with an interrupted framework or for particular structures like cancrinite; cavities may be filled with water oxygens, hydroxide anions or anions of the 6th or 16th and 17th group or other anionic complexes (Meier, 1986). In the literature one often finds the term 'zeolite' used to describe hydrated minerals with all sorts of frameworks (*i.e.* with O octahedra, O triangles *etc.*).

Observations on structures

For this study, we consider chiefly natural minerals with zeolite-type structures according to the *Atlas of Zeolite Structure Types* (Meier & Olson, 1987) (a full list of minerals as well as references to the structure refinements are given in Table 3). In these structures, cations *T* are characterized by high bond valence. Compared to the *T*—O bonds (bond strength above 0·5 valence units) the cavity cation—O bonds are weak with bond strengths below 0·5 valence units and often show coordination polyhedra with strong deformations.

Cavity cation coordination

In order to describe the structures, the coordination polyhedra were simply defined from a bond-length calculation according to the following two principles. Firstly, the geometrical aspect of the cavity cation polyhedron is important; one should not forget that, in ionic structures like zeolite-type structures, anions are large relative to cations; cations may be regarded as caught in anion cages or polyhedra. In parthéite, seven relatively short distances (2·33–2·61 Å) characterize the coordination polyhedron; with an eighth O atom at a distance of 3·08 Å a distorted cube is formed; there is no reason in this case to ignore this last atom. Secondly, around some cavity cations one may observe two polyhedra: one with short cation–anion distances and the other with clearly longer cation–anion distances; for the latter polyhedron, the bond valence can sometimes be neglected, since according to bond-valence calculations, the value is close to zero. In sodalite, the Na atoms are surrounded tetrahedrally by four O atoms with distances of 2·37 Å plus three others with distances of 2·73 Å; only the closest tetrahedron is considered.

Cavity anions

Cavities may enclose three kinds of anions (Fig. 1): water oxygens which are neutralized by $2H^+$ (zeolites); extra-framework anions which are negatively charged and which may, among others, be extra-framework O tetrahedra centered by S, W or other cations of charge 6+, or carbonate anionic groups (*i.e.* sodalites, cancrinites); framework hydroxides which interrupt the oxygen framework

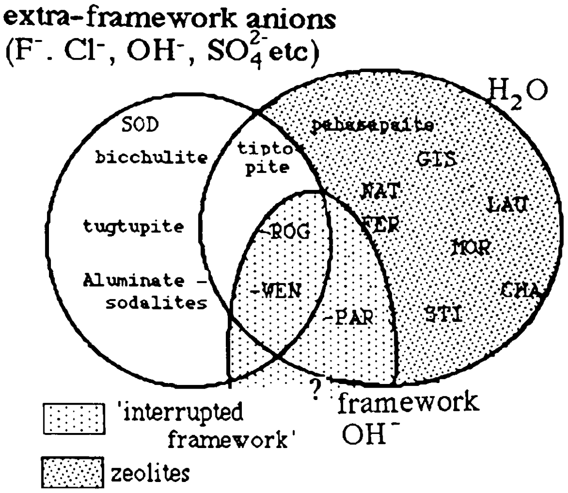


Fig. 1. Definitions for cavity anions and nomenclature used in this paper illustrated with examples (codes are according to the International Zeolite Association).

Table 1. *Crystallochemical rules, basic formulae and relations used in this paper*

Electrostatic valence rule (Pauling, 1960)

$$\sum e_i/\mathrm{CN}_i = |\mathrm{ch}_j|$$

where ch_j is the charge of anion j coordinated to cations i; e_i the cation charge; CN_i the cation coordination number; and e_i/CN_i the bond strength.

Extended electrostatic valence rule (Baur, 1970)
The value of the sum of the bond strengths received by the anions in a crystal is on average equal, with changed sign, to the (charge) of the anions.

Sharing coefficient (Zoltaï, 1960)
The average number of tetrahedra participating in the sharing of a corner in a structure

$$c_Z = 8a + 1 - a(a + 1)n/(4m')$$

where a is the integral part $[4m'/n]$; n the number of tetrahedron anions; and m' the number of cations centering tetrahedra.

Modified sharing coefficient (Coda, 1969)
The average number per tetrahedron of shared oxygens

$$C_C = 4(c_Z - 1).$$

Relation between polyhedra apices and anion composition (Engel, 1991)

$$n_\iota/m' = N_\iota/\iota$$

where n_ι is the number of anions coordinated to ι cations; m' the number of cations centering *i.e.* tetrahedra; and N_ι the number of apices coordinated to ι cations (for tetrahedra $\sum N_\iota = 4$).

Principle of maximal diversity (Engel, 1986)
The cations coordinated to each anion tend to be of as different a nature as possible, provided that the sum of the bond strengths calculated over each anion is close or equal to the charge of this anion.

Structural limits for zeolite structures (summary of Table 2 in Engel, 1989*a*)

(i) The number of framework O's which are 'valence deficient' (possible acceptors of H atoms) should be, on average per water oxygen, between one and two.

(ii) More than the half of the O atoms in the O framework should be 'valence deficient'.

(iii) A limit between zeolite structures *with a high water content* and *with a low water content* is defined by the ratio equal to one, of the numbers of water O's per 'overloaded' framework O's.

tetrahedra. Structures may contain several of these different anions (roggianite, wenkite).

Water oxygens. These may be linked to cavity cations by strong (or short) bonds. Through hydrogen bonds, they make further contacts with oxygen acceptors which belong to the O tetrahedra framework. In zeolites with a high water content, the water molecules may be free in large cages, in which case the water oxygens may act as acceptors of other H atoms. In a few zeolites (analcime), however, the H atoms are only linked to the water oxygens and no hydrogen bonds are observed (H atom–next O atom distance equal to 2·53 Å).

Hydroxides. When only bound to cavity cations, these act as extra-framework anions. When linked to framework oxygens, the H—O (donor) bonds interrupt the framework.

Other extra-framework anions. These are anions of the 6th, 16th or 17th group or complexes ZO_4 ($Z = S^{6+}$, W^{6+} *etc.*) or ZO_3 (Z = carbon). Their charge is compensated by the presence of more cavity cations in the structure than are needed by the framework. Furthermore, in these structures, the average charge of T atoms within the framework tends to be low. Thus, in order to balance the charge of all anions in the structure, the cavity cation coordination has to be low, which increases the bond strength for an anion coordination of four cations or less. The sum of cationic bond strengths, which the extra-framework anions 'receive' from the cavity cations, is observed to be slightly inferior or equal to the extra-framework anion charge.

Crystallochemical rules

Crystallochemical rules may be considered as substitutes for bonding mechanisms which are still unknown. Simple expressions are derived from observations of structures. An example of this type was given by Pauling (1960) *e.g.* the electrostatic valence rule for bond-strength definition. The rules or definitions used in this paper together with references are given in Table 1.

For zeolite-type structures, the sharing coefficient of Zoltaï (1960) or its modified form (Coda, 1969) (definitions in Table 1) is useful for calculating the average number of atoms T, which are linked to framework oxygens. For zeolite-type structures, this coefficient is equal to 2 (Zoltaï) or 4 (Coda) except for 'interrupted frameworks', for which the coefficient is slightly inferior to these values. The principle of maximal diversity (Table 1) was established based on observations of O coordinations in structures composed of Ca, Al, Si and H (Engel, 1986). It is related to the electrostatic valence rule as well and expresses the order in structures according to the anion (here chiefly oxygen) coordination. For zeolite structures (Engel, 1988), this is useful when looking for possible O coordinations, and in particular when evaluating the cavity cations coordinated to O atoms with reference to bond strength. Notice that this principle also covers the Loewenstein avoidance rule which excludes two tetrahedrally coordinated Al atoms bound to a common O atom and which becomes obsolete for Al-rich structures (*i.e.* aluminate sodalite, bicchulite).

A scheme for charge transfer (*Engel*, 1989*a*)

When a correction is applied to the bond strength in the function of the cation–anion bond length, *i.e.* the method of Donnay & Allmann (1970), one obtains a so-called bond valence. For instance, a short bond relative to a mean bond calculated over all central cation–anion bonds corresponds to a relatively high bond valence compared to the bond strength.

If, for a central anion, the sum of bond strengths calculated over the (cations i–central anion j) bonds is different from the charge on the anion or $\sum(e_i/\mathrm{CN}_i) - \mathrm{ch}_j| < > 0$, then this difference has to be compensated for. This can be expressed as a global cationic charge transfer from this central anion

Table 2. *Expected anion (mostly oxygen) coordinations in zeolite-type structures with water molecules or extra-framework anions*

O coordination	Observed values for $\sum(e_i/\mathrm{CN}_i) - \mathrm{ch}_j$	Anion coordination	Observed values for $\sum(e_i/\mathrm{CN}_i) - \|\mathrm{ch}_j\|$	ID
Framework oxygens				
Zeolites (see also Engel, 1989*b*)		With extra-framework anions		
$(Y\ Y)$	0·0	$(Y\ Y\ C)$	0·125 to 0·2	**k**
$(X\ Y)$	-0·25			**g**
$(X\ Y\ C)$	−0·2 to 0·25	$(X\ Y\ C)$	−0·2 to 0·25	**i**
$(X\ Y\ C\ C)$	0·0 to 0·2	$(X\ Y\ C\ C)$	0·0 to 0·1	**l**
		$(X\ X\ C)$	−0·25	**j**
		$(X\ X\ C\ C)$	0·2 to 0·2	**m**
Water molecules		Extra-framework anions		
(H H)		$(C\ C\ C\ C)$		
(H H C)		(H $C\ C\ C$)		
(H H $C\ C$)		$(Z\ C\ C\ C)$		
		$(Z\ C\ C)$		
		$(Z\ C)$		

Notes: (X) cations T with $e_X/4 < 1{\cdot}0$ or with $e_X \leq 3$ (Al^{3+}, Be^{2+} ...); (Y) cations T with $e_Y/4 \geq 1{\cdot}0$ and with $e_Y \geq 4$ (Si^{4+}, P^{5+}, Ge^{4+} ...); (C) cavity cations with $0{\cdot}125 \leq e_C/\langle\mathrm{CN}_C\rangle \leq 0{\cdot}5$; ($Z$) cations with $e_Z/\mathrm{CN}_Z > 1{\cdot}3$ ($Z = \mathrm{S}^{6+}$, W^{6+}, carbon...); (ID) average number of framework O atoms with specified coordination expressed in fractions.

through cations to (positive difference) or from (negative difference) neighbouring anions which determines more long or short central anion–cation distances respectively. The anions in the structure may be considered as electric poles according to the sum of cationic bond strengths around them. The so-called 'overloaded' anions transfer positive charges towards the anions which are deficient in positive valences (or 'valence deficient') through anion–cation–anion bonds. According to Baur's extended electrostatic valence rule, the sum of all these differences calculated over all anions of a structure is equal to zero.

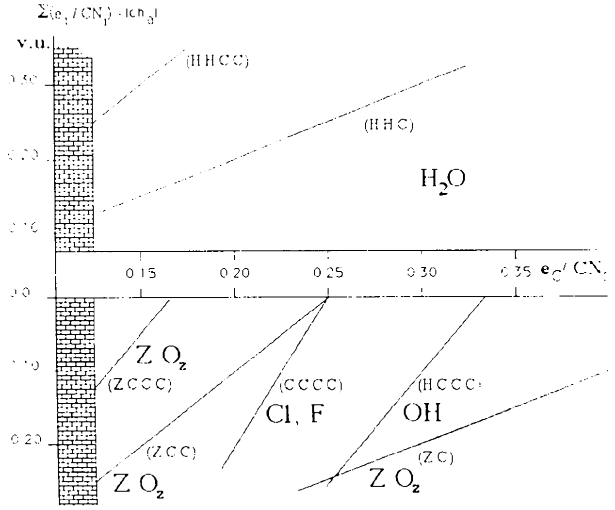


Fig. 2. Sum of bond strengths calculated around cavity anions $[\sum(e_i/\mathrm{CN}_i)]$ compared to the charge of the anions (ch_a) shown as a function of the bond strength of the cavity cation (e_C/CN_C). The bond strength of the extra cation ($Z = \mathrm{S}^{6+}$, W^{6+}, ...) equals 1·5 valence units. The charge of the water molecules is assumed to be equal to zero valence units.

For hydrogen atoms, which present an irregular coordination, we postulate a positive charge transfer through the O—H···O(acceptor) bonds in the direction of the oxygen acceptor. The valence of the H bond [or H···O(acceptor)] is supposed to be equal to the amount of charge transfered or potential difference. Since, in zeolites, the water oxygens belong mostly to the cavity cation polyhedra, H···O bonds are important for charge transfer from the cavity cation coordination sphere to the 'valence deficient' framework oxygens. This consideration allowed enunciation of structural limits for zeolites [Table 2 in Engel (1989*a*); summary in Table 1]. In structures which have hydroxides instead, since, according to observations, the cationic charge they 'receive' from the cavity cations is less than or equal to the charge of the OH^- group, hydrogen bonds are not expected.

Structural model

Expected anion coordinations (essentially oxygen coordinations) in zeolite-type structures with extra-framework anions or water molecules are established on the basis of crystallochemical rules (Table 2). Localization of cation–anion bonds follows the principle of maximal diversity and one does not expect more than four cations coordinated to oxygen atoms or other anions. In Table 2, for each anion coordination, maximal and minimal observed values for the sum of (cavity cation–anion) bond strengths compared to the charge of the anion $[\sum(e_i/\mathrm{CN}_i) - |\mathrm{ch}_j|]$ are given. For water molecules or extra-framework anions, values are given in Fig. 2.

The anion coordinations and values of the sum of the bond strengths compared to the oxygen charge are verified by observations on 39 structures of zeolites, sodalites and cancrinites (Table 3). Oxygen coordinations above four are observed for cavity anions: in amicite, water oxygens may be bound to three cavity cations and in cancrinite, hydroxide oxygens to four cavity cations. However, for framework oxygens, the model has been fully verified and can be used for further investigations of zeolite-type structures with a high chance of success.

Calculation of anion coordinations from chemical formulae

The numbers of framework oxygens coordinated to 2X or 2Y atoms

The X-atom composition may be expressed as:

$$x = x_1 + x_2$$

Table 3. *Framework oxygen coordinations expressed with ID's given in Table 2 for zeolite types (values either predicted from formulae or observed)*

Symbols and letters used in the table denote the following: *, with a different cavity anion coordination; *d*, structures with important disorders; *l*, less; *m*, more; *o*, observed data only; *u*, refinement not found; •, with water oxygens not bound to cavity cations.

Ref.	Mineral (natural or 'synthetic')	k	g	i	l	j	m	$\langle CN_C\rangle_{obs}$	$\langle CN_C\rangle_{predicted}$	Ideal chemical formula
With extra-framework anions										
(1)	'Aluminate sodalite'	0·0		0·0	0·0	0·0	1·0	8	8	$Ca_8(Al_{12}O_{24})(WO_4)_2$
				0·0	0·0	0·5^{l}	0·5^{m}		5·5* 7·0*	
(2)	'Basic sodalite'	0·0		1·0	0·0	0·0	0·0	4	4	$Na_8(Al_6Si_6O_{24})(OH)_2\ 2H_2O$
(3)	'Basic cancrinite'^{d}	0·0		0·25	0·75	0·0	0·0	≈7		$Na_{7\cdot5}(Al_6Si_6O_{24})(OH)_{1\cdot5}\ 5H_2O$
				0·5	0·5	0·0	0·0		6·73*	
(4)	Bicchulite	0·0		0·67	0·0	0·33	0·0	6	6	$Ca_2(Al_2SiO_6)(OH)_2$
				0·67	0·0	0·0	0·33		7	
(5)	Cancrinite	0·0		0·25	0·75	0·0	0·0	7·1	6·13-7·63	$(Na_7Ca)(Al_6Si_6O_{24})(CO_3)_{1\cdot5}\ 2H_2O$
(6)	Hauyne^{d}	0·0		1·0	0·0	0·0	0·0		4·5	$\approx(Na_5KCa_2)(Al_6Si_6O_{24})(SO_4)_{1\cdot5}$
(7)	Helvite	0·0		1·0	0·0	0·0	0·0	4	4	$Mn_3(Be_3Si_3O_{12})S$
(8)	Hsianghualite^{d}	0·0		0·0	1·0	0·0	0·0	6·4	6·4	$Li_{16}Ca_{24}(Be_{24}Si_{24}O_{96})F_{16}$
(9)	Lazurite^{d}	0·0		1·0	0·0	0·0	0·0		4	$Na_6Ca_2(Al_6Si_6O_{24})S_2$
(10)	Nosean^{d}	0·0		1·0	0·0	0·0	0·0		4	$Na_8(Al_6Si_6O_{24})SO_4$
				0·5^{l}	0·5^{m}	0·0	0·0		5·5*-7·5*	
(11)	Sodalite	0·0		1·0	0·0	0·0	0·0	4	4	$Na_8(Al_6Si_6O_{24})Cl_2$
(12)	Tiptopite^{o}	0·0		0·75	0·25	0·0	0·0	7·5		$\approx K_2Li_3Na_3(Be_6P_6O_{24})(OH)_2\ H_2O$
(13)	Tugtupite	0·33		0·33	0·33	0·0	0·0	5	5	$Na_8(Al_2Be_2Si_8O_{24})Cl_2$
'Interrupted framework'										
(14)	Chiavennite^{u}	0·47		0·20	0·20	+0·13 ?	(H Be Ca Ca)		7·5	$Ca_4Mn_4[Be_8Si_{20}O_{52}(OH)_8]\ 8H_2O$
(15)	Parthéite	0·06	0·35	0·35	0·12	+0·12	(H Al Ca)		8	$Ca_2[Al_4Si_4O_{15}(OH)_2]\ 4H_2O$
(16)	Roggianite^{d}	0·15	0·07	0·62	0·0	+0·13 ?	(H *T C C*)		8	$Ca_{14}(Na,K)[Be_5Al_{15}Si_{28}O_{90}(OH)_{14}](OH)_2\ 34H_2O$
						+0·02 ?	(*T C C*)			
(17)	Wenkite^{d}	≈0·2		≈0·3	0·44	+0·05 ?	(*T C C C*)		8	$(Ba,K)_4(Ca,Na)_6[Al_8Si_{12}O_{39}(OH)_2](SO_4)_3\ H_2O$ $(Ba,K)_4(Ca,Na)_6(Al_8Si_{12}O_{41})(OH)_2(SO_4)_3\ H_2O$
Zeolites with a low water content										
(18)	Analcime	0·33	0·0	0·67	0·0	0·0	0·0	6	6	$Na_{16}(Al_{16}Si_{32}O_{96})\ 16H_2O$
(19)	Bikitaite	0·33	0·17	0·50	0·0			4	4	$Li_2(Al_2Si_4O_{12})\ 2H_2O$
		0·33	0·0	0·67	0·0				6*	
(20)	Edingtonite	0·20	0·20	0·60	0·0			9·75		$Ba_2(Al_4Si_6O_{20})\ \approx 8H_2O$
		0·20	0·30	0·50	0·0				9	
(21)	Gonnardite^{o}	0·05	0·35	0·40	0·20			7		$Na_{6\cdot5}Ca_{1\cdot5}(Al_{9\cdot5}Si_{10\cdot5}O_{40})\ 12{\cdot}4H_2O$
(22)	Laumonite-leonhardite	0·33	0·33	0·33	0·0			8	8–6	$Ca_4(Al_8Si_{16}O_{48}) \le 16H_2O$
(23)	Mesolite^{o}	0·20	0·33	0·40	0·067			6·5		$Na_{16}Ca_{16}(Al_{48}Si_{72}O_{240})\ 64H_2O$
(24)	Natrolite	0·20	0·20	0·40	0·20			6	6	$Na_{16}(Al_{16}Si_{24}O_{80})\ 16H_2O$
(25)	Paranatrolite^{u}	0·20	0·20	0·40	0·20				7	$Na_{16}(Al_{16}Si_{24}O_{80})\ 24H_2O$
		0.20	0·20	0·60	0·0				6	
(26)	Scolecite	0·20	0·40	0·40	0·0			7	7	$Ca_8(Al_{16}Si_{24}O_{80})\ 24H_2O$
		0·20	0·48	0·32	0·0				6·2	
(27)	Tetranatrolite	0·20	0·20	0·40	0·20			6	6	$Na_{16}(Al_{16}Si_{24}O_{80})\ 16H_2O$
(28)	Thomsonite^{o}	0·0	0·40	0·50	0·10			8		$Na_4Ca_8(Al_{20}Si_{20}O_{80})\ 24H_2O$
(29)	Wairakite	0·33	0·33	0·33	0·0			6	6	$Ca_8(Al_{16}Si_{32}O_{96})\ 16H_2O$
(30)	Yugawaralite	0·50	0·25	0·25	0·0			8	8	$Ca_2(Al_4Si_{12}O_{32})\ 8H_2O$
Zeolites with a high water content										
(31)	Amicite^{o}	0·0	0·38	0·38	0·25			6·75*		$Na_4K_4(Al_8Si_8O_{32})\ 10H_2O$
(32)	Brewsterite	0·50	0·25	0·25	0·0			9	9	$Sr_2(Al_4Si_{12}O_{32})\ 10H_2O$
(33)	Chabazite^{o}	0·40	0·37	0·23	0·0			≈7·0		$\approx(Ca,Sr)_{1\cdot7}(Al_{3\cdot7}Si_{8\cdot3}O_{24})\ 13H_2O$
(34)	Cowlesite^{u}	0·20	0·60	0·20	0·0				8	$Ca_6(Al_{12}Si_{18}O_{60})\ 36H_2O$
(35)	Epistilbite	0·50	0·25	0·25	0·0			9·33	9·33	$Ca_3(Al_6Si_{18}O_{48})\ 16H_2O$
		0·50	0·33	0·17	0·0				8	
(36)	Gismondine	0·0	0·75	0·25	0·0			6·3•		$\approx Ca(Al_2Si_2O_8)\ 4H_2O$
		0·0	0·80^{l}	0·20^{m}	0·0				5·6 or more	
(37)	Gobbinsite	0·37	0·19^{l}	0·44^{m}	0·0			5	5 or more	$Na_5(Al_5Si_{11}O_{32})\ 11H_2O$
(38)	Goosecreekite	0·50	0·38	0·12	0·0			7		$Ca_2(Al_4Si_{12}O_{32})\ 10H_2O$
		0·50	0·31^{m}	0·19^{l}	0·0				8	
(39)	Harmotome^{o}	0·38	0·17	0·44	0·02			9·85•		$Ba_2Ca_{0\cdot5}(Al_5Si_{11}O_{32})\ 12H_2O$
(40)	Levyne^{o}	0·33	0·23	0·44	0·0			6·22•		$NaCa_{2\cdot5}(Al_6Si_{12}O_{36})\ 18H_2O$
(41)	Pahasapaite^{o}	0·0	0·38	0·63	0·0			5·7•		$(Ca,K,Na)_{11\cdot5}Li_8(Be_{24}P_{24}O_{96})\ 38H_2O$
(42)	Phillipsite^{o}	0·33	0·07	0·55	0·05			9·74•		$K_2Ca_{1\cdot5}Na_{0\cdot5}(Al_{5\cdot5}Si_{10\cdot5}O_{32})\ 12H_2O$
(43)	Stellerite^{d,o}	0·56	0·39	0·06	0·0			?	8	$Ca_4(Al_8Si_{28}O_{72})\ 28H_2O$
(44)	Stilbite^{o}	0·43	0·55	0·03	0·0			6·9•		$NaCa_4(Al_9Si_{27}O_{72})\ 30H_2O$
(45)	Willhendersonite^{o}	0·0	0·25	0·75	0·0			7•		$K_2Ca_2(Al_6Si_6O_{24})\ 10H_2O$

References to structure refinement: (1) Depmeier (1984); (2) Hassan & Grundy (1983); (3) Bresciani Pahor, Calligaris, Nardin & Randaccio (1982); (4) Sahl (1980); (5) Smolin, Shepelev, Butikova & Kobyakov (1981) and Jarchow (1965); (6) Löhn & Schulz (1968); (7) Holloway, Giordano & Peacor (1972); (8) *Section of Crystal Structure Analysis* (1973); (9) Hassan, Peterson & Grundy (1985); (10) Schulz (1970) and Hassan & Buseck (1989); (11) Hassan & Grundy (1984); (12) Peacor, Rouse & Ahn (1987); (13) Dano (1966); (15) Engel & Yvon (1984); (16) Galli (1980) and Passaglia & Vezzalini (1988); (17) Wenk (1973) and Merlino (1973); (18) Ferraris, Jones & Yerkess (1972); (19) Bissert & Liebau (1986); (20) Kvick & Smith (1983) and Mazzi, Galli & Gottardi (1984); (21) Mazzi, Larsen, Gottardi & Galli (1986); (22) *Structure Reports* (1967); (23) Artioli, Smith & Pluth (1986); (24) Torrie, Brown & Petch (1964); (26) Jodwig, Bartl & Fuess (1983); (27) Mikheeva, Pushcharovskii, Khomyakov & Yamnova (1986); (28) Pluth, Smith & Kvick (1985); (29) Takeuchi, Mazzi, Haga & Galli (1979); (30) Kvick, Artioli & Smith (1986); (31) Alberti & Vezzalini (1979); (32) Schlenker, Pluth & Smith (1977); (33) Alberti, Galli, Vezzalini, Passaglia & Zanazzi (1982); (35) Alberti, Galli & Vezzalini (1985); (36) Artioli, Rinaldi, Kvick & Smith (1986); (37) McCusker & Baerlocher (1985); (38) Rouse & Peacor (1986); (39) Rinaldi, Pluth & Smith (1974); (40) Merlino, Galli & Alberti (1975); (41) Rouse, Peacor & Merlino (1989); (42) Rinaldi, Pluth & Smith (1974); (43) Galli & Alberti (1975); (44) Galli (1971); (45) Tillmanns, Fischer & Baur (1984).

where x_1 and x_2 represent the 'amount' of X atoms involved in, one and two O—X bonds ($X = \mathrm{Al}^{3+}$, Be^{2+}...) respectively. Using the expression which relates anion composition to polyhedra apices (Engel, 1991; see Table 1), this becomes:

$$x = n_{x1}/4 + 2n_{x2}/4$$

where n_{x1} and n_{x2} represent the number of framework oxygens with respectively one and two O—X bonds.

With $n_x = n_{x1} + n_{x2}$, this equation becomes:

$$n_x = 4x - n_{x2}. \qquad (1a)$$

Similarly, for Y atoms:

$$n_y = 4y - n_{y2} \qquad (1b)$$

where n_{y1} and n_{y2} are the numbers of framework oxygens with, one and two O—Y bonds ($Y = \mathrm{Si}^{4+}$, P^{4+}...) respectively. The principle of maximal diversity is expressed with logical operators by:

$$(n_{x1} = n_{y1}) \text{ AND } (n_{x2} = 0 \text{ OR } n_{y2} = 0).$$

It follows:

$$n_x + n_{y2} = n_y \text{ XOR } n_y + n_{x2} = n_x,$$

whence

$$n_{y2} = n_y - n_x \text{ XOR } n_{x2} = n_x - n_y,$$

and with (1) the numbers of O atoms linked whether to 2 X atoms or to 2 Y atoms (n_{x2}, n_{y2}) becomes:

$$n_{x2} = 2(x - y) \qquad (2a)$$

$$n_{y2} = 2(y - x). \qquad (2b)$$

The numbers of framework oxygens ($\mathrm{O_{fw}}$) *with defined numbers of* C—$\mathrm{O_{fw}}$ *bonds*

The total number of cavity cation bonds in a structure is expressed by the general formula:

$$q\langle \mathrm{CN}_c\rangle = n\langle \mathrm{CN}_{o-c}\rangle + a\langle \mathrm{CN}_{a-c}\rangle \qquad (3)$$

where $\langle \mathrm{CN}_c\rangle$ is the average coordination number of cavity cations (C), $\langle \mathrm{CN}_{o-c}\rangle$ the average number of C—$\mathrm{O_{fw}}$ bonds per framework oxygen, $\langle \mathrm{CN}_{a-c}\rangle$ the average number of C—cavity anion bonds per cavity anion, q the cavity cation composition, n the number of framework oxygens, and a the cavity anion composition (water oxygens included).

For water oxygens which are neutral, according to the scheme for charge transfer, an effective negative charge may be estimated from the valences of the hydrogen bonds. A maximal value for this bond is equal to 0·20 valence units (Baur, 1972), hence a maximal effective charge of 0·40 valence units per water oxygen, which is for the case of structures in which all H atoms are bound to framework oxygens (most zeolites with a low water content; Table 3). From observations, one knows that the cavity anion charge available for cavity cations (ch_{a-c}) may not be entirely compensated by the bond strengths of the cavity cations ($e_C/\mathrm{CN_C}$). The number of cavity cations coordinated to cavity anions (CN_{a-c}) may therefore, for each anion, be calculated to a good approximation by using (see Fig. 3):

$$\mathrm{CN}_{a-c} = \text{integral part } [\mathrm{ch}_{a-c}/(e_C/\mathrm{CN_C})]. \qquad (4)$$

Then in order to use (3), one should first calculate an average value for CN_{a-c}. However, for structures with single types of cavity anion and of cavity cation, this average value is obtained directly from (4). A value for the average coordination number of framework O's bound to C atoms ($\langle \mathrm{CN}_{o-c}\rangle$) is then calculated with (3). For structures with extra-framework anions, this parameter gives a value between 1 and 2 (compare the O coordinations in Table 2), so that, for n_3 and n_4, the numbers of framework O's coordinated to respectively three and four cations are:

$$n_3 = n(2 - \langle \mathrm{CN}_{o-c}\rangle) \qquad (5a)$$

and

$$n_4 = n(\langle \mathrm{CN}_{o-c}\rangle - 1). \qquad (5b)$$

For zeolites, the CN_{o-c}'s may have values between 0 and 2 (see Table 2), but the average value is below 1. Consequently:

$$n_3 + 2n_4 = n\langle \mathrm{CN}_{o-c}\rangle \qquad (6a)$$

$$n_2 - n_4 = n(1 - \langle \mathrm{CN}_{o-c}\rangle) \qquad (6b)$$

with $n_2 \geq n_4$ and with $n_4 = 0$ for zeolite structures with a cavity cation bond strength above 0·2 valence units. According to Engel (1989*b*, p. 600), the number of oxygen atoms coordinated to three cations, when calculated over a whole structure, should be greater or at least equal to the number of O atoms with coordinations of 2 or 4. This con-

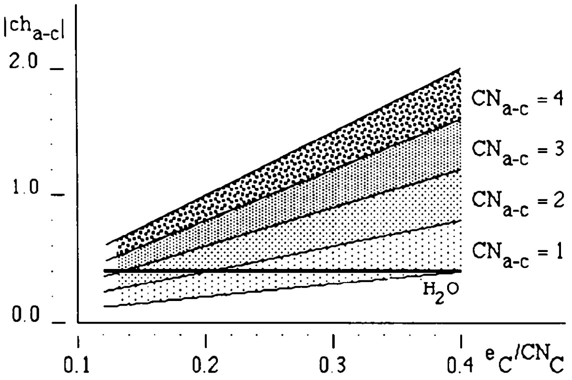


Fig. 3. Partial coordination (central cavity anion—cavity cations) (CN_{a-c}) calculated as a function of the bond strength of cavity cations (e_C/CN_C) and of the charge of cavity anions available for these bonds (ch_{a-c}). Bold line: maximum expected effective charge of waters (0·4 valence units), supposed to be equal to the maximum transferred charge through hydrogen bonds.

sideration is restricted to framework oxygens coordinated to T atoms or cavity cations, and, as shown in Fig. 4, it allows the n parameters to be calculated as a function of $\langle CN_{o-c}\rangle$.

With extra-framework anions:

	$n_{x_2} \ge 0$	$n_{y_2} \ge 0$
$e_C/CN_C \ge 0.25$ v.u.	$\frac{n_{x_2}}{n} = \mathbf{m} + \mathbf{j} \quad \mathbf{j} = \frac{n_{x_2} - n_4}{n}$ $\frac{n_3}{n} = \mathbf{i} + \mathbf{j} \quad \mathbf{i} = \frac{n_4 + n_3 - n_{x_2}}{n}$ $\frac{n_4}{n} = \mathbf{m}$ condition $\mathbf{j} \le \mathbf{m} + \mathbf{i}$ or $\mathbf{j} \le 0.5$	none according to sum of bond strengths, (Y Y C) is not possible (see table 2)
$e_C/CN_C < 0.25$ v.u.	$\frac{n_{x_2}}{n} = \mathbf{m}$ $\frac{n_3}{n} = \mathbf{i}$ $\frac{n_4}{n} = \boldsymbol{\ell} + \mathbf{m} \quad \boldsymbol{\ell} = \frac{n_4 - n_{x_2}}{n}$ condition $\boldsymbol{\ell} \ge \mathbf{m} + \mathbf{i}$ or $\boldsymbol{\ell} \ge 0.5$	$\frac{n_{y_2}}{n} = \mathbf{k}$ $\frac{n_3}{n} = \mathbf{i} + \mathbf{k} \quad \mathbf{i} = \frac{n_3 - n_{y_2}}{n}$ $\frac{n_4}{n} = \boldsymbol{\ell}$ condition $\boldsymbol{\ell} \ge \mathbf{i}$ or $\boldsymbol{\ell} \ge 0.5$

Zeolites:

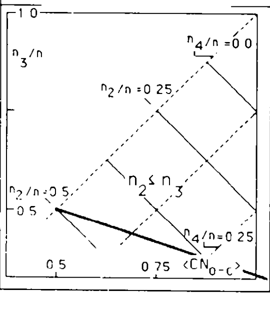
$e_C/CN_C \ge 0.2$ v.u.	? (X X) not expected in structures with H_2O only	$\frac{n_{y_2}}{n} = \mathbf{k}$ $\frac{n_2}{n} = \mathbf{k} + \mathbf{g} \quad \mathbf{g} = \frac{n_2 - n_{y_2}}{n}$ $\frac{n_3}{n} = \mathbf{i}$ condition for $e_C/CN_C \ge 0.25$ $\mathbf{g} \ge \mathbf{i}$
$e_C/CN_C < 0.2$ v.u.		$\frac{n_{y_2}}{n} = \mathbf{k}$ $\frac{n_2}{n} = \mathbf{k} + \mathbf{g} \quad \mathbf{g} = \frac{n_2 - n_{y_2}}{n}$ $\frac{n_3}{n} = \mathbf{i} \quad \frac{n_4}{n} = \boldsymbol{\ell}$ condition $\mathbf{g} + \mathbf{i} \ge \boldsymbol{\ell}$

Fig. 4. The fraction of the framework oxygens with the coordinations specified in Table 2 (see ID's) calculated as a function of the fractions of framework O's coordinated to 2, 3 or 4 cations (n_2/n, n_3/n or n_4/n) and of the fractions of framework O's bound to 2 X and 2 Y atoms (n_{x2}/n, n_{y2}/n, respectively). The graph below shows the relation between the n parameters and the average framework O coordination to cavity cations ($\langle CN_{o-c}\rangle$) for zeolites with $e_C/CN_C < 0.2$ valence units; structures are expected above the bold line for which $n_2 = n_3$ and for which $\langle CN_{o-c}\rangle \ge 0.5$.

Fig. 5 shows the relationship between the average partial coordination (O_{fw}—cavity cations) ($\langle CN_{o-c}\rangle$) and n_{x2}/n respectively n_{y2}/n. This graph may be used to find the numbers of framework oxygens (n) with the coordinations given in Table 2 from the specified compositions. A detailed account of this graph is given by the equations of Fig. 4. In this figure, ID's **k**, **g**, **i**, **l**, **j** and **m** are fractions of the numbers of framework oxygens with the coordinations given in Table 2.

Prediction of coordinations in structures

For structures with cavity cations with similar bond strengths (all above or below 0·2 valence units for zeolites; all above or below 0·25 valence units for structures with extra-framework anions), it is now possible to calculate the numbers of anions with specified coordinations. The principle of structure prediction is as follows: after calculation of the numbers of framework O's linked either to 2 X atoms or to 2 Y atoms [equation (2)], values for the ID's (or fraction of framework oxygens with the coordinations given in Table 2) are taken from the dotted fields in Fig. 5 and then tested according to

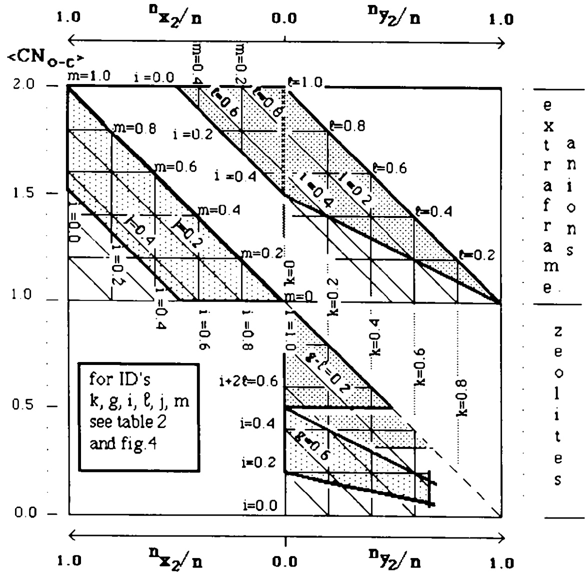


Fig. 5. Framework oxygen coordinations (ID's) shown as a function of the T-atom compositions [expressed by n_{x2} or n_{y2}; equation (2)] and the average partial coordination of framework oxygens to cavity cations ($\langle CN_{o-c}\rangle$). Limitations of dotted fields are given by conditions of Fig. 4. For zeolites, no more than 66·7% n_{y2} and no more than four water molecules per X atom are expected (lowest limit). Coarse dotted and dense dotted fields are for structures with bond strengths of cavity cations above and below 0·25 valence units, respectively. Zeolite structures with cavity cations of bond strength just above 0·2 valence units may fall within the dotted field between both frames.

the resulting cavity cation and cavity anion coordinations and bond strengths [equations (3) and (4)]. The values obtained are compared with the observed values in Table 3. For instance, for sodalite, if the bond strength of Na atoms is greater than or equal to 0·25 valence units then only one structure is expected with all framework O's bound to (Al Si Na); Cl coordination equals four (Table 2) and following (3), the Na coordination equals four with a bond strength equal to 0·25 valence units. In case a higher Na coordination number (or a Na bond strength below 0·25 valence units) is foreseen, according to (4) the Cl coordination should be more than four. For nosean instead, different coordinations for the Na atoms as well as for the cavity anion might be possible, hence several solutions in Table 3. Several predictions may also be made for zeolites, but the observed structure usually corresponds to the predicted structure with the lowest number of 'valence deficient' O atoms compared to the water O content, as long as this fraction is not less than one [compare condition (i) in Table 1]. For zeolites with a high water content, (4) may not be valid since in most of these structures, which are often highly disordered, water oxygens may not be bound to cavity cations; there is as yet no means of predicting this coordination. In Table 3, predictions are given for several disordered or unknown structures (basic cancrinite, hauyne, hsiangshualite, lazurite, nosean).

According to the conditions defined by this analysis, the variability of the cavity cation coordinates is restricted (compare predicted and observed values in Table 3). This coordination is in fact regarded as a consequence of an electrical equilibrium between framework and cavity atoms.

'Interrupted framework'

Until now, among zeolite types, only four minerals have shown a structure built of a three-dimensional tetrahedral framework whose linkage is interrupted (parthéite, chiavennite, wenkite, roggianite; Table 3). All of these have cavity cations of charge 2+ and present dense structures with a relatively high amount of cavity cation—O bonds (values for $\langle CN_{o-c} \rangle$ from 0·71 for parthéite up to 1·54 for wenkite). With the exception of parthéite, these structures are not clearly known yet. In Table 3, therefore, most probable values for the O_{fw} coordinations are given, which should be considered with caution. One notices different O coordinations from those given in Table 2. Framework interruption may in fact be caused either by an excess of *C* bonds towards framework oxygens (probably wenkite) or by the presence of OH^- groups (parthéite, probably chiavennite) or both (probably roggianite).

When caused by OH^- groups, according to the principle of maximal diversity, the framework interruption occurs most probably on tetrahedra centered by *X* cations. When calculated from the coordinations given in Table 2, it results in:

$$2(XY...) + (HH...) \rightarrow (YY...) + 2(HX...),$$

so that the total number of framework oxygens is increased by half the number of hydroxides in the framework and the number of O's bound to two *Y* atoms is increased as well. In this case, the presence of these hydroxides may be related to water oxygens with too many cavity cation bonds and with too high bond strengths. In the same manner, in zeolites with cavity cations of charge 1+, water molecules may be bound to two cavity cations at once, which increases the load to be transferred through the hydrogen bonds and frees other O atoms for acceptance of hydrogen bonds (*i.e.* natrolite). This is improbable for zeolites with cavity cation bond strengths above 0·25 valence units since the load to be transferred should become higher than the hydrogen bond valence. On one hand, this extra coordination occurs elsewhere in the cavity cation polyhedron; this explains the fact that in parthéite the O atoms are coordinated to (Si Al Ca Ca) with one long Ca—O bond, as mentioned above. On the other hand, the over-coordinated water molecules may 'split' into OH groups. Thus, since O coordination (H H *C C*) is

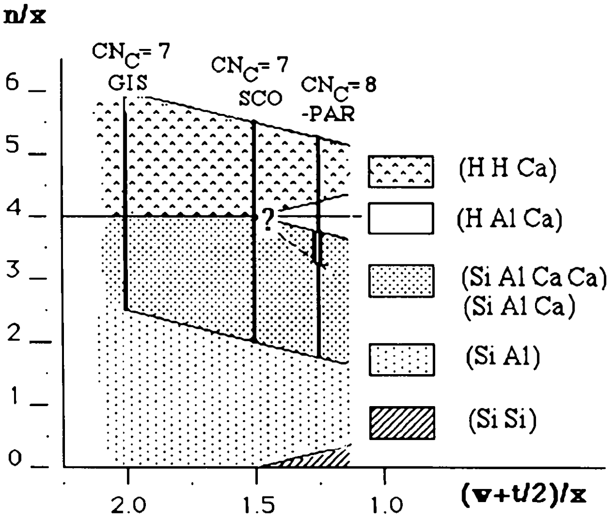


Fig. 6. Oxygen coordinations in structures or part of a structure with composition $Ca_{x/2}[Al_xSi_xO_{4x-t/2}(OH)_t]$ wH_2O. The numbers of O atoms given in the ordinate are relative to the numbers of Al atoms in the structure (*n*/*x*). In scolecite (SCO), there is one more O atom coordinated to (Si Si). Framework interruption is shown in relation to the low water or hydroxide contents [(*w* + *t*/2)/*x*]. Thin lines: extrapolation for O coordination contents; single or double bold lines: one or two Ca atoms coordinated to O atoms.

not stable:

$$2\,(\mathrm{Si\ Al}) + (\mathrm{H\ H}\ C\ C) \rightarrow (\mathrm{Si\ Si}) + 2\,(\mathrm{H\ Al}\ C)$$

and in order to balance the hydrogen bonds;

$$4\,(\mathrm{Si\ Al}\ C) \rightarrow 2\,(\mathrm{Si\ Al}) + 2\,(\mathrm{Si\ Al}\ C\ C).$$

In Fig. 6, O coordinations observed in parthéite are compared with those in gismondite and scolecite. Framework interruption is shown in this figure as a consequence of very low water content. With still less waters, there may be more (Al—O) bonds in the structures either with Al atoms coordinated to six oxygen atoms [lawsonite: Ca $\mathrm{Al_2^{[6]}(Si_2O_7)(OH)_2H_2O}$] or with more Al in the structure balanced by extra-framework hydroxide groups (bicchulite).

In beryllosilicates, interruption of the framework by $\mathrm{OH^-}$ groups may be frequent, because of the low charge of the Be atoms in tetrahedra (roggianite, chiavennite). In the case of wenkite, the interruption is probably due to O atoms with (Si C C C) coordination ($C = \mathrm{Ca^{2+}}$, $\mathrm{Ba^{2+}}$), which increases the number of O atoms with (Si Al ...) coordinations. This may explain the extra-framework anions in the structure.

A structural chemical definition of zeolite-type structures

According to anion coordinations, two major groups of zeolite-type structures may be distinguished. Minerals with zeolite structures are characterized by porous structures with cavities or cages filled by water molecules beside cavity cations. As long as the water content is not too high, refinements reveal ordered structures, whereas disorder is frequently observed in structures of zeolites with a high water content. Several of these structures could not, for this reason, be included in this study. Since the difference in the sum of the bond strengths compared to the anion charge should not exceed 0·25 valence units, that is, when P or Be atoms are in the tetrahedra, neither (Si Be) nor (P P) coordinations may be expected: *e.g.* pahasapaite with equal contents of Be and P atoms.

Zeolite-type minerals with extra-framework anions (*i.e.* $\mathrm{F^-}$, $\mathrm{Cl^-}$, $\mathrm{[SO_4]^{2-}}$, $\mathrm{[WO_4]^{2-}}$, $\mathrm{[CO_3]^{2-}}$, $\mathrm{[OH]^-}$) are characterized by structures with cages, in which all framework oxygens bind one or two cavity cations. In structures with X atoms and $e_X = 2$ (*i.e.* $\mathrm{Be^{2+}}$), (X X...) coordinations should be avoided as long as the sum of all cationic bond strengths is less than 1·75 valence units. In the same manner, (Y Y...) coordinations should be avoided for Y atoms with $e_Y = 5$ (*i.e.* $\mathrm{P^{5+}}$). Minerals observed are from the sodalite or cancrinite structure types, as well as from other zeolite structure types [analcime: hsianghualite; edingtonite: $\mathrm{K_3(Al_2Si_3O_{10})Cl}$] (Ghose, Hexiong & Weidner, 1990).

The structural limits defined previously for zeolites (Table 1) have also been verified for the beryllophosphate pahasapaite. In contrast to zeolites, as soon as extra-framework anions are located in the structure, more 'overloaded' O atoms than 'valence-deficient' O atoms are observed in the framework. This determines a borderline between zeolites and zeolite types with extra-framework anions. Zeolite types with an interrupted framework have a very low cavity anion content. Other silicates with a very low water content (scapolites, milarites, cordierites, cymrite) may not satisfy our conditions for zeolites, since most of the O atoms which form the Al (or low valence) tetrahedron may be overloaded (unpublished results). One known exception to condition (ii) is the zeolite bikitaïte which shows an exceptionally dense framework (Brunner & Meier, 1988; Engel, 1989*b*).

The above limitations for zeolite types may, in turn, be applied to structures with O polyhedra other than tetrahedra in the framework. For petarasite [$\mathrm{Na_5(Zr_2^{[6]}Si_6O_{18})(Cl,OH).H_2O}$; Ghose & Wan, 1980], the framework oxygens are shared between one Zr and one Si atom leading to the same O coordinations as in Table 2. The same applies to hilgardite [$\mathrm{Ca_2(B_3^{[4]}B_2^{[3]}O_9)Cl.H_2O}$; Ghose & Wan, 1979]. Both minerals fulfill the conditions for zeolite-type structures according to anion coordinations. Might these minerals show zeolite properties?

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Structure of Pentaammineaquacobalt(III) Hexacyanochromate(III), $[Co(NH_3)_5(H_2O)][Cr(CN)_6]$, by Neutron Diffraction at 2·0 K

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Abstract

$M_r = 370·2$, rhombohedral, $R\bar{3}$, $a = 7·282\,(2)$ Å, $\alpha = 97·71\,(2)°$, $V = 374·6\,(2)$ Å^3, $Z = 1$, $D_m(295\text{ K}) = 1·59\,(1)$, $D_x = 1·64\text{ g cm}^{-3}$, neutron diffraction, $\lambda = 1·1760\,(2)$ Å, $\mu = 2·05\text{ cm}^{-1}$, $F(000) = 27·4 \times 10^{-14}$ m, $T = 2·0$ K, $R(F) = 0·029$ for 643 unique reflections, $\chi = 2·17$. The water molecule is dis-