

NATURAL ZEOLITES

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Preface

Contemporary mankind faces an increasingly serious danger of pollution of the air and water of our planet by toxic wastes.

The serious task of the protection of civilization against ecological catastrophe confronts the scientists and specialists of the world. In this respect, undoubted interest resides in zeolites which can be utilized in various environmental protection systems against pollution with great success because of unique adsorptive, molecular sieve, ion-exchange and catalytic properties. Such interests in zeolites greatly increased in the 1960s and 1970s, when large industrial sized deposits of zeolites were discovered.

The discovery of stratified sedimentary zeolites, together with their comparative simplicity of mining, relatively low cost and more or less worldwide distribution gave easy access to these minerals for large-scale utilization. In particular this included uses for drying and purification of gases and effluents of different origin in order to trap toxic compounds and recover valuable components, for the disposal of radioactive wastes, for more rational and safe utilization of mineral fertilizers and toxic chemicals in agriculture, and so on.

This book, a joint effort of researchers from states of the former USSR and from Bulgaria, does not pretend to completely clarify all of the problems concerning the properties and utilization of natural sedimentary zeolites. Rather it considers the most important questions concerning mineralogical classification of zeolite structures, the genesis of natural sedimentary zeolites, and their occurrence. The natural sedimentary zeolites are considered as microporous adsorbents, ion-exchangers and catalysts; various uses in industry, agriculture, and in environment protection are also dealt with.

Obviously, our book is not free from deficiencies, and the authors would be happy to receive any comment. If this book is in some way useful for readers interested in the properties and utilization of natural sedimentary zeolites, the efforts of the authors will have been worthwhile.

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Names for the successor states and institutions of the former USSR are those that were in use at the time the book was being written.

1

The mineralogy of the zeolites

At present the zeolite group includes more than 40 naturally occurring species, and is the largest group of minerals among the silicates. Before the 1960s, zeolite minerals were thought to be mainly distributed in hydrothermal veins and geodes in basalts (Fig. 1.1), andesites and other volcanic rocks. Zeolites in such settings form large, well-shaped crystals and druses. Due to the usual small size of the veins and because of polyminerality, these deposits have no practical importance, but samples of vein origin have been used to establish the properties of the minerals and the possibility of their utilization in industry. All known zeolites have been found in hydrothermal veins; some of them are major rock forming species.

Only in recent decades, first in Japan, and later in the USA and Europe, has a wide distribution of zeolites in certain sedimentary rocks been established. These deposits differ markedly from the primary type. They are frequently monomineralic, of huge dimensions and suitable for industrial mining. Zeolite crystals in sedimentary rocks, however, are usually microscopic in size (Fig. 1.2).

1.1. CRYSTAL CHEMISTRY OF THE ZEOLITES

According to Smith [1] a zeolite is an aluminosilicate with a skeletal structure, containing voids occupied by ions and molecules of water having a considerable freedom of movement that leads to ion-exchange and reversible dehydration.

The primary building block of the zeolite framework is the tetrahedron, the centre of which is occupied by a silicon or aluminum atom, with four atoms of oxygen at the vertices. Each oxygen atom is shared between two tetrahedra. Hence, the tetrahedra form a continuous framework. Substitution of Si^{4+} by Al^{3+} defines the negative charge of the framework, which is compensated by monovalent or divalent cations located



Fig. 1.1. Chabazite crystals of hydrothermal vein origin.

together with water molecules in structural channels. Cations in the channels are substituted easily, and therefore they are termed exchange or extra-framework cations, unlike Si and Al which are not exchanged under ordinary conditions; the latter are termed tetrahedral (T) or framework cations.

The idealized chemical formula of the zeolites is of the type $M_{x/n}[Al_xSi_yO_{2(x+y)}] \cdot pH_2O$ where M is (Na, K, Li) and/or (Ca, Mg, Ba, Sr), n is cation charge; $y/x = 1$ to 6, $p/x = 1$ to 4. It is also convenient to express the zeolite composition by so-called oxide formulas of the type $M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$. The oxide formula of the widely distributed natural zeolite clinoptilolite is thus $(K, Na, 1/2Ca)_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 8H_2O$. Unit cell contents can be expressed as $(K_2, Na_2, Ca)_3[Al_6Si_{30}O_{72}] \cdot 24H_2O$, or $(K_2, Na_2, Ca)_3[Al_6Si_{30}O_{72}] \cdot 24H_2O$. The composition of the tetrahedral framework is usually given in square brackets.

The Si/Al ratio in natural zeolites lies within the limits of 1 to 6. The lower limit is determined by Löwenstein's rule, according to which an AlO_4 tetrahedron cannot associate with another AlO_4 tetrahedron by a common oxygen atom; at $Si/Al = 1$, the silicon and aluminum tetrahedra alternate to form the ordered framework. Ordered location of Si and Al is also possible at other Si/Al ratios. The upper limit of the

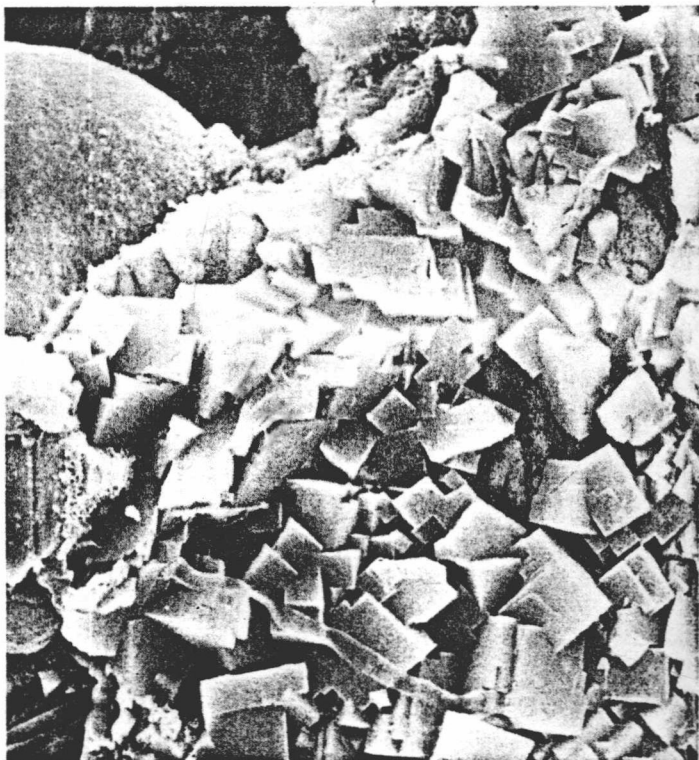


Fig. 1.2. Clinoptilolite crystals in zeolitic tuff from Eastern Rhodopes, Bulgaria (SEM, $\times 600$).

Si/Al ratio in the natural zeolites reaches 5 to 6 (clinoptilolite, mordenite, ferrierite, dachiardite). In synthetic zeolites the silicon can be substituted by germanium, and the aluminum by gallium, iron, chromium, boron, etc, but in natural specimens only Be and Fe is observed in tetrahedral sites, in addition to Si and Al.

The Si/Al ratio can vary considerably within the limits of one structural type, depending upon the composition of original solutions and conditions of crystallization. Zeolites are also characterized by complex substitutions of the type $(\text{Na}, \text{Al}) \rightleftharpoons \text{Si}$ and $(\text{Ca}, \text{Al}) \rightleftharpoons \text{Na}, \text{Si}$, and by the simple substitutions $\text{Ca} \rightleftharpoons 2\text{Na}$, $\text{Na} \rightleftharpoons \text{K}$, and so forth.

The water content varies within certain limits depending upon the character of the exchange cations and conditions of crystallization. Under ordinary conditions the water molecules completely fill the free volume of channels and voids in the zeolite structure. The free inner volume of the zeolite can be calculated by measuring the volume of the water released under heating *in vacuo*. Experience shows that the volumes calculated by this method agree well with structural data.

Chemical formulae, limits of variability of chemical composition and some crystallographic and structural data for known zeolite mineral species are given in Table 1.1. Reliable chemical analyses are presented in Gottardi and Galli's monograph [2].

Table 1.1—Basic data for the various zeolite groups

Date of discovery	Group (SBU), mineral, unit cell content	Si/Al range, exchangeable cations	Structure type	Symmetry, space group	Unit cell constants, nm	Total pore volume, %
Analcime group (4 or 6)						
1784	analcime	1.8–2.8	ANA	cubic	$a = 1.373$	20
(1801)*	$\text{Na}_{16}\text{Al}_6\text{Si}_{32}\text{O}_{96} \cdot 16\text{H}_2\text{O}$	$\text{Na} \gg \text{Ca} \approx \text{K}$		$Ia3d^b$		
1955	wairakite	~ 2	ANA	monoclinic	$a = 1.369, b = 1.364$ $c = 1.356, \beta = 90.5^\circ$	21
	$\text{Ca}_8\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot 16\text{H}_2\text{O}$	$\text{Ca} \gg \text{Na}$		$I2/a$		
1943	viseite		ANA	cubic $a = 1.365$		20
	$\text{Na}_2\text{Ca}_{10}\text{Al}_{20}\text{Si}_8\text{P}_{10}\text{O}_{60}(\text{OH})_{36} \cdot 16\text{H}_2\text{O}$					
Laumontite group (4)						
1978	laumontite*	2	LAU	monoclinic	$a = 1.504, b = 1.317$ $c = 0.771, \beta = 133.2^\circ$	32
(1808)	$\text{Ca}_4\text{Al}_8\text{Si}_{16}\text{O}_{48} \cdot 16\text{H}_2\text{O}$			$C2/m$		
1952	yugawaralite	2.2	YUG	monoclinic	$a = 0.673, b = 1.395$ $c = 1.003, \beta = 111.5^\circ$	29
	$\text{Ca}_2\text{Al}_4\text{Si}_{12}\text{O}_{32} \cdot 8\text{H}_2\text{O}$	some Na		Pc		
1822	brewsterite	2.6–3.0	BRE	monoclinic	$a = 0.677, b = 1.751$ $c = 0.774, \beta = 94.3^\circ$	30
	$(\text{Sr}, \text{Ba}, \text{Ca})_2\text{Al}_4\text{Si}_{12}\text{O}_{32} \cdot 10\text{H}_2\text{O}$	$\text{Sr} > \text{Ba} > \text{Ca}$		$P2_1/m$		
1980	goosecreekite	3.0	BRE	monoclinic	$a = 0.740, b = 1.744$ $c = 0.729, \beta = 105.6^\circ$	32
	$\text{Ca}_2\text{Al}_4\text{Si}_{12}\text{O}_{32} \cdot 10\text{H}_2\text{O}$			$P2$		
Natrolite group (4-1)						
1758	natrolite	1.5	NAT	orthorhombic	$a = 1.830, b = 1.863,$ $c = 0.66$	22
(1803)	$\text{Na}_{16}\text{Al}_6\text{Si}_{24}\text{O}_{80} \cdot 16\text{H}_2\text{O}$	some Ca, K		$Fdd2$		
1969	tetranatrolite	1.6–1.7	NAT	tetragonal	$a = 1.310, c = 0.663$	22
(1980)	$\text{Na}_{14.4}\text{Ca}_{0.4}\text{Al}_{15.5}\text{Si}_{24.7}\text{O}_{80} \cdot 16\text{H}_2\text{O}$	some K		$I42d$		
1813	mesolite	1.4–1.6	NAT	orthorhombic	$a = 1.841, b = 5.665$ $c = 0.655$	26
(1816)	$\text{Na}_{14}\text{CaAl}_{16}\text{Si}_{24}\text{O}_{80} \cdot 16\text{H}_2\text{O}$	$\text{Ca}:\text{Na} \geq 1$		$Fdd2$		
1801	scolecite	1.5	NAT	monoclinic	$a = 0.653, b = 1.897$ $c = 0.978, \beta = 108.9^\circ$	31
(1813)	$\text{Ca}_4\text{Al}_8\text{Si}_{12}\text{O}_{40} \cdot 12\text{H}_2\text{O}$			Cc		
1896	gonnardite	1.1–1.4	NAT	orthorhombic	$a = 1.335, b = 1.335$ $c = 0.665$	31
	$\text{Na}_3\text{Ca}_2\text{Al}_9\text{Si}_{11}\text{O}_{40} \cdot 12\text{H}_2\text{O}$	$\text{Na}:\text{Ca} = 2 - 6$		or tetragonal		
1801	thomsonite	1.0–1.1	THO	orthorhombic	$a = 1.305, b = 1.309,$ $c = 1.322$	31
(1820)	$\text{Na}_4\text{Ca}_8\text{Al}_{20}\text{Si}_{20}\text{O}_{80} \cdot 24\text{H}_2\text{O}$	$\text{Ca}:\text{Na} = 1.6 - 2.0$		Pmm		
1835	edingtonite	1.5	EDI	tetragonal	$a = 0.958, c = 0.652$	36
	$\text{Ba}_2\text{Al}_4\text{Si}_6\text{O}_{20} \cdot 8\text{H}_2\text{O}$	some K, Ca, Na		$P4_2/m$ or orthorhombic $P2_12_12_1$	$a = 0.955, b = 0.967$	

Mordenite group (5-1)		Phillipsite group (4-doubly connected)	
1864	mordenite (Na ₂ ,Ca)Al ₈ Si ₄₀ O ₉₆ ·28H ₂ O	1824	phillipsite K ₂ (Ca,Na ₂) ₂ Al ₆ Si ₁₀ O ₃₂ ·12H ₂ O to K ₂ (Na ₂ ,Ca)Al ₆ Si ₁₀ O ₃₂ ·10H ₂ O
1905	dachiardite (Na ₂ ,K ₂ ,Ca ₂)Al ₆ Si ₂₀ O ₄₈ ·12H ₂ O	1755	harmotome Ba ₂ (Ca _{0.5} Na)Al ₅ Si ₁₁ O ₃₂ ·12H ₂ O
1826	epistilbite Ca ₄ Al ₅ Si ₁₈ O ₄₈ ·16H ₂ O	(1801)	merlinoite (K,Nal ₃)(Ba,Ca) ₂ Al ₉ Si ₃ O ₆₄ ·24H ₂ O
1981	ferrierite (Na ₂ ,K ₂ ,Ca,Mg) ₃ Al ₆ Si ₃₀ O ₇₂ ·20H ₂ O	1816	gismondine Ca ₄ Al ₆ Si ₆ O ₃₂ ·16H ₂ O
1957	bikitaite Li ₂ Al ₂ Si ₄ O ₁₂ ·2H ₂ O	1962	garronite NaCa _{2.5} Al ₆ Si ₁₀ O ₃₂ ·13H ₂ O
		1982	gobbsinite Na ₄ (Ca,Mg,K ₂)Al ₆ Si ₁₀ O ₃₂ ·12H ₂ O
		1979	amicite Na ₄ K ₄ Al ₈ Si ₈ O ₃₂ ·10H ₂ O
		1974	mazzite K ₂ Mg ₂ Ca _{1.5} Al ₉ Si ₇ O ₇₂ ·28H ₂ O
		1960	paulingite (K ₂ Na ₂) ₈ Al ₁₇₂ Si ₅₀₀ O ₁₃₄₄ ·700H ₂ O
			(K ₂ Na ₂) ₈ Al ₁₇₂ Si ₅₀₀ O ₁₃₄₄ ·700H ₂ O

Table 1.1—continued

Date of discovery	Group (SBU), mineral, unit cell content	Si/Al range, exchangeable cations	Structure type	Symmetry, space group	Unit cell constants, nm	Total pore volume, %
Erionite group (6 + (6-6))						
1890 (1898)	erionite (K ₂ Na ₂ CaMg ₄ Al ₈ Si ₂₈ O ₇₃ ·28H ₂ O)	3-4 Mg to 1, K 1-3, Na 1-4, Ca 0.3-2.5 2.2-2.6	ERI	hexagonal <i>P6₃/mmc</i>	<i>a</i> = 1.315 <i>c</i> = 1.505	38
1890	offretite (K ₂ Ca ₂ Mg _{2.5} Al ₅ Si ₁₃ O ₃₆ ·15H ₂ O)	K ~ 1, Ca ≈ Mg	OFF	hexagonal <i>P6₃mm</i> 2	<i>a</i> = 1.329, <i>b</i> = 0.758	40
1825	levyne NaCa _{2.5} Al ₈ Si ₁₂ O ₃₆ ·18H ₂ O	1.6-2.0 some K	LEV	rhombohedral <i>R3m</i>	<i>a</i> = 1.084, <i>a</i> = 75.95°	42
Chabazite group (6-6)						
1772	chabazite ^c (Ca ₂ Na ₂ K ₂)Al ₄ Si ₈ O ₂₄ ·12H ₂ O	1.5-4.0 some Sr, Ba	CHA	rhombohedral or triclinic	<i>a</i> = 0.941, <i>a</i> = 94.3° <i>a</i> = 0.941, <i>b</i> = 0.942	44
(1972)	(K ₂ Na ₂ Ca) _{1.5} Al ₃ Si ₉ O ₂₄ ·10H ₂ O ^d willhendersonite		CHA	<i>P1</i> triclinic	<i>c</i> = 0.942, <i>a</i> = 94.2° <i>a</i> = 0.920, <i>b</i> = 0.918, <i>c</i> = 0.949	40
1984	Ca ₂ K ₂ Al ₆ Si ₆ O ₂₄ ·10H ₂ O				<i>a</i> = 92.7°, <i>β</i> = 92.4°, <i>γ</i> = 90.1°	
1808 (1825)	gmelinite (Na ₂ Ca) ₄ Al ₈ Si ₁₆ O ₄₈ ·22H ₂ O	2.0-2.2 Na > Ca	GME	hexagonal <i>P6₃/mmc</i>	<i>a</i> = 1.375, <i>c</i> = 1.006	41
Faujasite group (6-6) or β-cage [6⁸4⁶]						
1842	faujasite (Na ₃ Ca) ₂ Al ₃₈ Si ₁₃₄ O ₃₈₄ ·240H ₂ O	2.2-2.6 Ca ≈ Na	FAU	cubic <i>Fd3m</i>	<i>a</i> = 2.460	51
Unknown structure						
1979	partheite Ca ₈ Al ₁₆ Si ₁₆ O ₆₄ ·16H ₂ O	1.0 some K, Na		monoclinic <i>C2/c</i>	<i>a</i> = 2.159, <i>b</i> = 0.878 <i>c</i> = 0.931, <i>β</i> = 91.3°	32
1975	cowlesite Ca ₆ Al ₁₂ Si ₁₈ O ₆₀ ·30H ₂ O	~ 1.5 some Na		orthorhombic	<i>a</i> = 1.127, <i>b</i> = 1.525 <i>c</i> = 1.261, <i>β</i> = 91.5°	47
1984	perillite ^e K ₉ Na(Ca,Sr)Al ₁₂ Si ₂₄ O ₇₂ ·15H ₂ O	2	LTL(?)	hexagonal	<i>a</i> = 1.849, <i>c</i> = 0.751	20

^aThe year it received its present name. ^bOften pseudocubic (*Ibca*, *I4₁/acd*). ^cExposed to air, it loses 2H₂O and turns reversibly into leonhardite. ^dBa-predominant phillipsite is wellsite. ^eThe term *herschelite* is used for chabazites with Na > Ca.

In the zeolite structure three relatively independent components are found: the aluminosilicate framework, exchangeable cations, and zeolitic water. This independence is expressed in the existence of the same structure with varying components. For example, cations can exchange and water molecules can be removed completely or be substituted by other molecules. The independence is relative, since any change of one component causes change of the other two. While the cations are mobile, the framework is more or less deformed and stressed upon dyhydration; the distribution of water molecules depends upon the character, the quantity and distribution of cations and this in turn is defined by the density and distribution of anionic sites in the structure.

1.1.1. The aluminosilicate framework

The aluminosilicate framework is the most conserved and stable component and defines the structure type. The topology of the framework, the numbers and distribution of charges (aluminum sites) and stacking faults are basically formed at the crystal growth stage and define a series of technologically important properties of zeolites. Framework topology forms the basis of contemporary classification of the zeolites.

For a mathematical description of the topology, the atomic pattern is reduced to its simplest characteristics. The tetrahedron is considered as a structural point, *i.e.* only the centre of the tetrahedron is taken into account. The centres of neighbouring tetrahedrons are connected with straight lines (T-T) and the whole framework is represented as a three-dimensional lattice; each centre is connected with four others, and the oxygen atoms are located near, but not on the connecting line (T-T). After such simplification, separate polygonal and polyhedral sub-units are easily located in the structure.

On the basis of structural sub-units such as combinations of parallel four- or six-membered rings and Archimedean polyhedra, one classification of zeolites was suggested [3]. Later, Meyer [4] introduced the notion of "secondary building units" (SBU). An SBU is the simplest configuration of tetrahedra out of which a given tetrahedral framework can be built. Figure 1.3 shows these structural units: four-, six- or eight-membered ordinary rings (4, 6, 8), double rings (4-4, 6-6, 8-8) and complexes (4-1, 5-1, 4-4-1).

From any SBU one can construct numerous frameworks, including those of all the natural and synthetic zeolites found to date. Figure 1.4 shows two linked SBUs (4-4-1), which are found in minerals with the heulandite and stilbite structures.

The structural type of any given zeolite is defined by the topology of the framework. At present the nomenclature used (and respective three-letter codes for structural types) are those designated by a Commission of IUPAC (Table 1.2). In each structural type there are several structures with similar topology differing by various orderings of tetrahedron cations, small deviations from ideal symmetry, and the composition and distribution of the exchangeable cations. Fine stereoscopic pictures of all structural types are given in the "Atlas of Zeolite Structure Types" [5].

Table 1.2.—Basic data for zeolite structure types

IUPAC code	Maximum topological symmetry	Secondary building units	Polyhedral cage type	D ^a	N ^b	Channel systems in hydrated zeolite free apertures nm	direction	Average framework density, T/nm ³ of apertures
ANA	<i>Ia3d</i>	4 or 6		1	6	0.26	<111>	18.6
BIK	<i>Cmcm</i>	5-1		1	8	0.32 × 0.49	[001]	20.2
BRE	<i>P2₁/m</i>	4		2	8	0.23 × 0.50	[100]	17.5
					8	0.27 × 0.41	[001]	
CHA	<i>R3m</i>	6-6 or 4	[8 ⁶ 6 ² 4 ¹²], 6 ² 4 ⁶	3	8	0.36 × 0.37	1 [0001]	14.5
DAC	<i>C2/m</i>	5-1		2	10	0.37 × 0.67	[010]	17.5
					8	0.36 × 0.48	[001]	
EDI	<i>P4₂/m</i>	4-1		3	8	0.35 — 0.39	<100>	16.6
					8	variable	[001]	
EPI	<i>C2/m</i>	5-1		2	10	0.3, 0.53	[100]	17.7
					8	0.37 × 0.44	[001]	
ERI	<i>P6₃/mmc</i>	6 or 4	[6 ² 4 ⁶], [8 ⁶ 6 ² 4 ¹²], [6 ² 4 ⁶]	3	8	0.36 × 0.52	1 [0001]	16.0
FAU	<i>Fd3m</i>	6-6 or 4		3	12	0.74	<111>	12.9
FER	<i>IMM</i>	5-1	[12 ⁶ 6 ² 4 ¹⁸], [6 ⁸ 4 ⁶]	2	10	0.43 × 0.55	[001]	17.7
					8	0.34 × 0.48	[010]	
GIS	<i>I4₁/amd</i>	4 or 8		2	8	0.31 × 0.44	[100]	15.3
					8	0.28 × 0.49	[010]	
GME	<i>P6₃/mmc</i>	6-6 or 4	[8 ³ 6 ² 4 ⁹], [6 ² 4 ⁶]	3	12	0.70	[0001]	14.6
					8	0.36 × 0.39	1 [0001]	
HEU	<i>C2/m</i>	4-4-1		2	10	0.44 × 0.72	[001]	17.2
					8	0.41 × 0.47	[001]	
					8	0.40 × 0.50	[100]	
LAU	<i>A2/m</i>	4		1	10	0.40 × 0.56	[100]	17.7
LEV	<i>R3m</i>	6	[8 ³ 6 ⁶ 4 ⁹], [6 ² 4 ⁶]	2	8	0.33 × 0.53	1 [0001]	15.3
LTL	<i>P6₃/mm</i>	6	[6 ² 4 ⁶]	1	12	0.71	[0001]	16.4
MAZ	<i>P6₃/mmc</i>	4 or 5-1	[8 ³ 6 ² 4 ⁹]	1	12	0.74	[0001]	16.1

MER	$I4/mmm$	4 or 8-8	3	8	0.31×0.35 0.35×0.35 0.34×0.51 0.33×0.33 0.67×0.70 0.29×0.57 0.26×0.39 variable 0.64 0.36×0.52 0.39 0.39 0.42×0.44 0.28×0.48 0.33 0.41×0.62 0.27×0.57 0.26×0.39 0.26×0.39 variable 0.31×0.33 0.31×0.35	$[100]$ $[010]$ $[001]$ $[001]$ $[001]$ $[010]$ $\langle 101 \rangle$ $[001]$ $[0001]$ $\perp [0001]$ $\langle 100 \rangle$ $\langle 100 \rangle$ $[100]$ $[010]$ $[001]$ $[100]$ $[101]$ $[101]$ $[010]$ $[001]$ $[100]$ $[001]$	16.0	
MOR	$Cmcm$	5-1	2	12				17.2
NAT	$I4_1/amd$	4-1	3	8				17.8
OFF	$P6m2$	6	3	12	$[6^2 4^6]$, $[6^3 4^6]$ $[8^3 6^2 4^9]$ $[8^2 4^8]$, $[8^6 4^{12}]$ $[8^6 8_4 1^2]$			15.5
PAU	$Im3m$	4	3	8				15.3
PHI	$Cmcm$	4	3	8				15.8
STI	$Fmmn$	4-4-1	2	10				16.3
THO	$Pmma$	421	3	8				17.7
YUG	$C2/m$	4	2	8				18.3

^aOne-, two- or three-dimensional system. ^bNumber of tetrahedra in the rings.

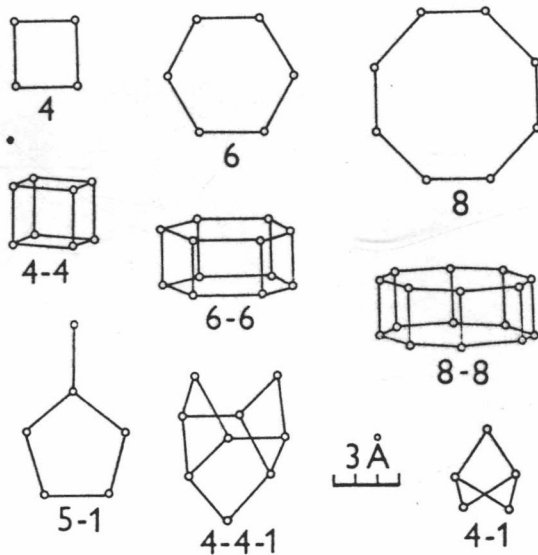


Fig. 1.3. The secondary building units (SBU) of the zeolite structures.

Apart from SBUs, various numbers and shapes of rings according to the components of the tetrahedra, as well as different channels and voids in the zeolite frameworks (Table 1.2), can be identified. Generally, voids are polyhedral in shape (Fig. 1.5). Certain zeolite structures can be elaborated by alteration of such polyhedra. In this sense, the cancrinite, sodalite and gmelinite cells can also be considered as SBUs.

Inside the polyhedra rather large voids are found. In faujasite a 26-hedron spherical free volume 1.18 nm in diameter is found, whereas that in sodalite has a diameter of 0.66 nm. In chabazite the inner void is 1.1 nm along the c axis and 0.65 nm perpendicular to it. It can also be seen from Figure 1.5 that the polyhedra have "windows" made by 6-8- and 12-membered rings, through which small molecules

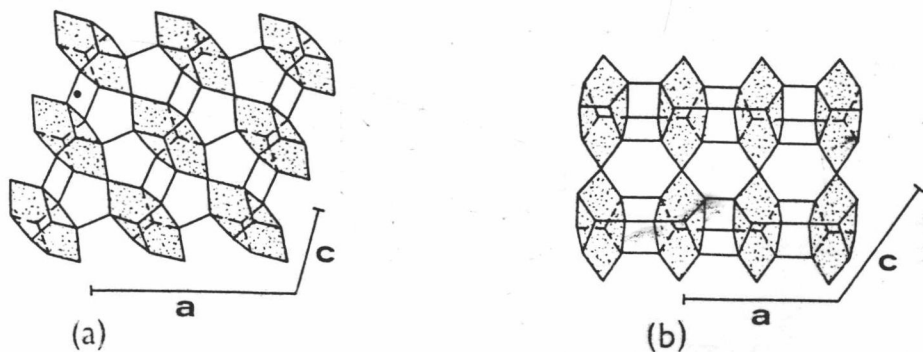


Fig. 1.4. Arrangement of the 4-4-1 units in the framework structures of (a) heulandite and (b) stilbite.