

The Properties of Coordination Sequences and Conclusions Regarding the Lowest Possible Density of Zeolites

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The topology of framework structures may be characterized by coordination sequences. It is shown that the information contained in these sequences is expressible in terms of two or three parameters. From diagrams involving such parameters it may be concluded that zeolites with densities considerably lower than those presently known would either contain three-membered rings or would have *T*-atoms connected to more than three four-membered rings. There are arguments against the realization of such properties, and zeolites of essentially lower densities will possibly not be found.

Introduction

Frameworks may be characterized by a notation which we call CS (C for coordination, connection, or cascade, S for sequence or series). In principle, as shown in Fig. 1, the CS is an infinite sequence of numbers, $CS = \{N_k\} = N_1, N_2, \dots, N_k, \dots$, indicating the number of atoms in "sphere" k which are connected to atoms in "sphere" $k-1$ ($1-4$). Since sequences of numbers are impractical to handle, algebraic expressions with a minimum number of parameters have been sought which express the CS exactly, or as a good approximation, and which may be derived from simplified models of crystal frameworks. Topological features are thus described by parameters which are suited to statistical examinations. Among other data, the CS evaluated by Meier and Möck (2) served as "experimental material."

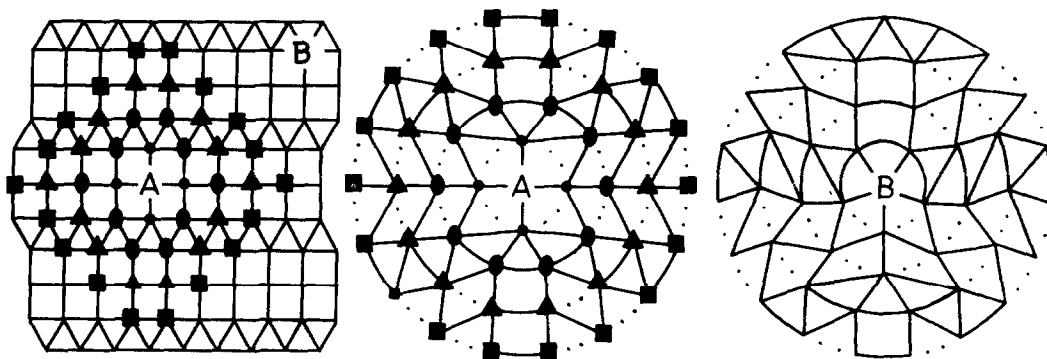
The CS is also valuable for storage and retrieval purposes. To avoid cases where topologically different frameworks might have the same CS, the *T*-atoms may be

distinguished according to the links leading to atoms of the previous, the same and the following sphere, as shown in Fig. 1, or the CS of the edge-to-vertex dual may be given in addition.

The evaluation of frameworks on the basis of atomic positions depends on the definition of coordination and is not discussed here. In many cases the procedure using the largest gap in the sequence of interatomic distances (5, 6) may be applied.

Approximation of CS by Equations

In the case of faujasite with $CS = 4, 9, 16, 25, 37, \dots$, a correlation between CS and the square of the "step number k " is evident. In particular, the CS of sodalite and of the primitive cubic, body-centered cubic, and face-centered cubic lattice complex may be represented by the equation $N_k = ak^2 + 2$, where a equals 2, 4, 6, and 10, respectively. For cristobalite (diamond), the equation $N_k = 2.5k^2 + 1.75$ renders values too high by 0.25 if k is odd and too low by 0.25 if k is even. The second derivative of a quadratic



$$A: \{N_k\} = 4, 10, 14, 18, 24, 28, \dots = (2 \leftarrow, 2 \leftarrow), (2 \leftarrow, 4 \leftarrow, 4 \leftarrow), (2 \leftarrow, 4 \leftarrow, 8 \leftarrow) \dots$$

$$B: \{N_k\} = 5, 9, 14, 19, 23, 28, \dots = (1 \leftarrow, 2 \leftarrow, 2 \leftarrow), (1 \leftarrow, 2 \leftarrow, 2 \leftarrow, 2 \leftarrow, 2 \leftarrow) \dots$$

$$AB_2: \{\bar{N}_k\} = 4.67, 9.33, 14.00, 18.67, 23.33, 28.00 \dots$$

FIG. 1. Planar example demonstrating the figurative meaning of the CS. The framework is redrawn to show the atoms of "sphere k " which are connected to atoms of "sphere $k-1$."

expression is a constant; by analogy, the second differences between subsequent numbers of the CS in these particular examples (except faujasite) are constants, or have a constant period. N_k may be represented in all cases by the expression $(\alpha k + \beta)^2 + 2$, either approximately or exactly. For example, for quartz, $\alpha = 1.896$, $\beta = -0.55$, and the calculated values deviate from the true values given in Table I by ± 0.5 or less.

Parameter β and the number 2 may be neglected for higher values of the CS and the above equation then becomes $N_k = \alpha^2 k^2$.

TABLE I
COORDINATION SEQUENCES AND FRAMEWORK DENSITIES OF SOME SILICATES

	N_1	N_2	N_3	N_4	N_5	$T/1000 \text{ \AA}^3$
Feldspar (mean)	4.0	10.0	21.0	38.0	56.5	23.3
Coesite (mean)	4.0	10.0	22.5	47.0	82.5	29.0
Cristobalite	4	12	24	42	64	23.0
Tridymite	4	12	25	44	67	23.0
Quartz	4	12	28	52	82	26.7

This relation may be derived from a simplified model of frameworks. The increase of the numbers N_k may be compared with the growth of a crystal structure as shown in Fig. 1. Starting at origin A, the "seed" is stepwise surrounded with shells of further atoms. The thickness of each additional shell is approximately the same since it depends mainly on the (constant) bond length; the total diameter of the crystal is therefore linearly connected with step number k . The increase in volume for a given increase in diameter of a three-dimensional body depends on the square of its diameter, which is in line with the dependence of N_k on k^2 . Parameter α reflects essentially the number of atoms per unit volume. Analogously, in two-dimensional structures, N_k depends on k linearly.

For the first few numbers of the CS, there is a correlation between N_k and k^3 . It holds better for zeolites than for other structures and is mentioned here since it illustrates the particular topological properties of the zeolites. Very roughly speaking, a zeolite is a sponge consisting of holes and of dense

interhole material. The first steps of growth of the CS produce trumpet-like rods of dense material extending into various directions of space (in the previously held view, space was assumed to be uniformly filled with matter). The length of the trumpets grows linearly with step number k , and the diameter grows faster. The volume of the trumpets increases faster than the volume of the seed in the previously held view. The expression $N_k = (\gamma k + \delta)^3$ turns out to be a reasonable approximation for the first five numbers of the CS; for higher numbers it becomes poor. Figuratively, the trumpet-like rods touch each other after a few steps and they can no longer grow in the same way. The parameter γ has properties similar to those of α .

Plots Involving CS-Parameters and Conclusions Regarding Hypothetical Zeolites

The foregoing discussion reveals that the CS contains essentially three pieces of information: (1) the coordination number, $CN = N_1$, which is 4 for all silicates mentioned here, (2) N_2 as a measure of the size and the number of the smallest rings, and (3) α as a measure of the increase of subsequent CS numbers. Since $N_k \approx \alpha^2 k^2$ for higher numbers of the CS, any higher number is a measure similar to α . Therefore, N_2 and N_5 may be used to characterize the topology of the silicates discussed here.

As a simple application of the CS parameters, the zeolites may be listed in the order of increasing N_2 for classification purposes (2). In the order of increasing N_5 , the list looks similar, except that it is better correlated with the density; thomsonite, edingtonite, and natrolite appear now in the middle of the list instead of at the beginning.

As a more interesting application, the parameters N_2 and N_5 may be correlated with the number of T -atoms contained in 1000 \AA^3 (framework density ρ) which is a characterization for the silicates often used in the literature. Figure 2A shows a plot of N_5

versus ρ . It seems plausible that the zeolites will be found at the low-density side of the field of representatives while dense silicates such as quartz and coesite will appear near the high-density side. The representatives near the tentatively drawn border of lowest density are fairly well separated into groups having smallest rings of the same size: The *size of the smallest rings* seems to be of more importance for obtaining the *lowest possible* framework density than the *manner of their connection*. At higher density the separation of the groups is blurred; ρ and N_5 depend in a complex manner on ring size as well as on ring connection. In view of this grouping, it may be concluded by extrapolation that hypothetical zeolites whose density would be considerably lower than the density of existing structures would contain three-membered rings. In models, each T -atom of an existing framework may actually be replaced by a unit of four T -atoms placed at the corners of a tetrahedron-like polyhedron. By repetition of this replacement procedure [suggested by Heesch and Laves for the case of sphere packings (7)], structures with three-membered rings may be built, whose density has no lower limit. The packings of spheres of lowest density known so far contain also three-membered rings (4, 7, 8). Variations of density with chemical composition do not essentially affect the groupings in Fig. 2 because the borders are more or less parallel to the ρ -axis.

In Fig. 2B, ρ is plotted versus N_2 . A positive correlation may be expected since ρ and N_5 are correlated (see Fig. 2A and the earlier discussion), and since N_2 and N_5 are correlated members of the same CS. One may therefore tentatively bound the field of representatives by a lower border line with a positive slope. By extrapolation, it may be concluded from Fig. 2B that hypothetical zeolites with a density considerably lower than existing examples would have values of N_2 lower than 9. This requires either two or more three-membered rings, or four or more

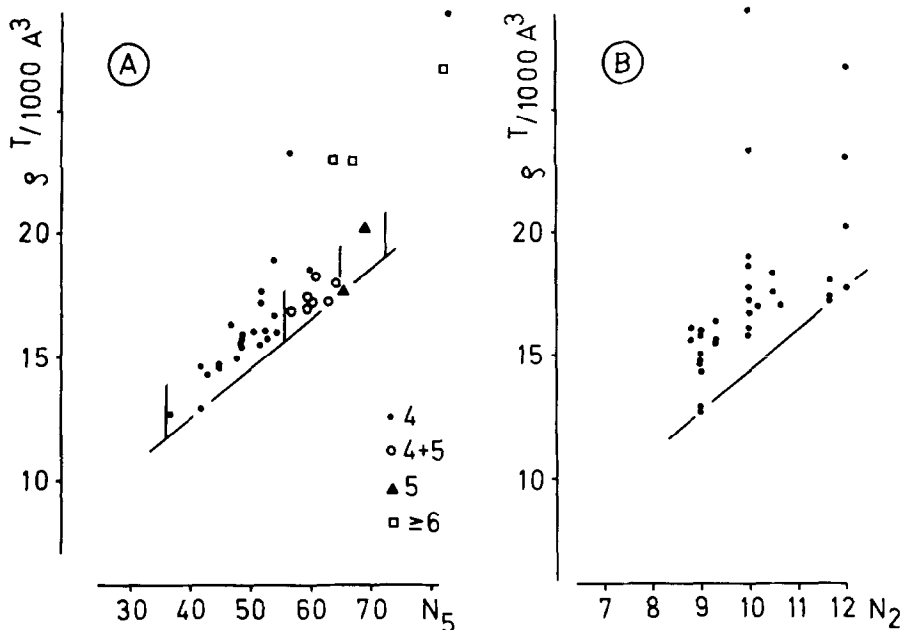


FIG. 2. Plot of ρ (average values) versus N_5 and N_2 , respectively, for silicates of Table I and for zeolites listed by Meier and Möck (2). Low density borders are tentatively drawn. (A) The representatives near the border are grouped according to the size of smallest rings connected to a T -atom; at lower density, 3-rings may be expected. (B) At lower density, $N_2 < 9$ may be expected which requires 3-rings or more than three 4-rings to be connected to a T -atom.

four-membered rings, to be connected to a T -atom. In fact, it is possible to construct models with vanishing density if further hexagonal prisms are inserted between truncated octahedra and hexagonal prisms in the structure of faujasite (leading to four 4-rings connected to a T -atom), or if further cubes are inserted between truncated octahedra and cubes in the structure of Linde type A (leading to five 4-rings connected to a T -atom).

The conclusions might be used as a guide for the synthesis of low-density zeolites, but the chances of success are doubtful for various reasons: (a) In a framework, three-membered rings are unfavorable because of strain; (b) if T -atoms are connected to more than three four-membered rings, three or even all four neighbors of a T -atom will be placed within a rather narrow solid angle on one side of that T -atom, which is unfavorable for electrostatic reasons; and (c) the

models of vanishing density mentioned above contain increasing numbers of topologically different types of T -atoms, which is against the rule of parsimony. Hence, inasmuch as pattern recognition, extrapolation, and chemical reasonings are admissible methods, considerations involving the CS notation indicate constraints on potential zeolite structures. This result encourages one to carry out further work on the CS notation.

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