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A FIRST-ORDER MARKOV-CHAIN MODEL OF ZEOLITE CRYSTALLIZATION[1]

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Abstract—A method using a finite, first-order Markov chain is presented to estimate rate constants for zeolite formation from experimental nuclear magnetic resonance (NMR) data on the abundance of different silica oligomers. An experimental design is suggested by which this method can be implemented. The method uses weighted least squares to estimate transition probabilities from aggregate NMR data. Rate constants, equilibrium constants, and free energies of elementary zeolite-forming reactions can be estimated. Hypothetical zeolite-forming reactions can also be modeled. An example of modeling, using hypothetical data, shows how zeolite formation can result from reactions involving mainly silica cyclic tetramers.

Key Words—Crystallization, Markov-chain model, Rate constants, Silica oligomers, Zeolites.

INTRODUCTION

The mechanism by which zeolites and other aluminosilicates form from relatively dilute solutions in nature is not well understood. Many explanations have been offered of the crystallization of synthetic zeolites from gels, but a gel stage does not seem to be involved in the crystallization of most natural zeolites. Therefore, the mechanisms that have been proposed and the kinetics presented may be applicable for synthetic zeolites, but are probably not applicable to the formation of natural zeolites under geologically reasonable conditions. Because of the similarity of various silica oligomers, e.g., cyclic tetramers, to zeolite structural units, several investigators (Hayhurst and Sand, 1977; Hawkins 1981; Donahoe and Liou, 1985) have suggested that these oligomers are essential building blocks of natural zeolites. Donahoe and Liou, in particular, presented strong evidence for the validity of this mechanism and showed that ^{29}Si nuclear magnetic resonance (NMR) spectra can provide information on the distribution of the various oligomers during the crystallization process. One difficulty with the data obtained to date (see Cary *et al.*, 1982; Donahoe and Liou, 1985), is that only the aggregate distribution of the various silica oligomers at one particular time is reported. No data showing rate constants for zeolite-forming reactions involving specific silica or aluminosilicate oligomers have been presented. The purpose of the present paper is to propose a method whereby such aggregate data can be decomposed to yield estimates of rate constants for individual elementary reactions. The proposed method uses a Markov chain model for the silica oligomerization and zeolite crystallization processes.

Markov chains have been widely applied to simulate geologic processes (Harbaugh and Bonham-Carter, 1970; Lin and Harbaugh, 1984; Davis, 1986), polymer formation (Lowry, 1970; Carman *et al.*, 1977; Bruns *et al.*, 1981; Cheng, 1982), and chemical kinetics (Formosinho and Miguel, 1979). Transition probabilities for a first-order Markov chain can be estimated from the aggregate data using the method of Kalbfleisch and Lawless (1984). These estimated transition probabilities can then be decomposed to yield rate constants for elementary oligomerization reactions. Extension of the method to include zeolite crystallization appears possible. No actual numerical values of rate constants are reported here, because the data necessary for their calculation by this method are not available. The present paper draws on the above applications and applies them to the problem of silica polymerization and zeolite crystallization.

MARKOV CHAIN MODEL

A first-order Markov chain is a form of stochastic process involving discrete steps in time (space) in which the probability of the transition from one state to the next state in the chain depends upon the immediate previous state. This dependence is called the Markov property. A Markov-chain model is intermediate between a purely random process and a completely deterministic one. The basic properties of Markov chains are well described in the preceding references and in Kemeny and Snell (1976) and Strang (1976); only a brief, essentially non-mathematical treatment of Markov chains is given here.

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The starting point for a Markov chain analysis is the construction of a transition matrix. This matrix is N × N, where N is the number of states, e.g., different silica oligomers, the elements of which are the probabilities for the transitions from one state to another. This means that the sum of the elements of each row equals 1.00.

To put first-order Markov chain analysis into more familiar geologic terms (Harbaugh and Bonham-Carter, 1970), assume that in a stratigraphic section four lithologic units exist consisting of sandstone, shale, limestone, and coal, in a cyclic depositional sequence. Assume also that one records the number of transitions from each rock unit to the next in progression upwards from the bottom of the section. In other words, the number of times that a coal is followed by a sandstone, shale, limestone is recorded, etc. In this example, the matrix is 4 × 4, each row represents the particular state (rock unit) being observed, and the column entries for that row are the number of times that particular rock unit is followed by another type of rock. If the counts in each row of this matrix of observed transitions are divided by the sum of the counts in that row, the entries are probabilities of transition from one state to the next. Thus, if one were in a "coal" state, meaning that the coal row is being used, the entries in that row represent the probabilities of a coal being followed stratigraphically by a shale, sandstone, or limestone. In this paper, the corresponding transition probabilities are the probabilities that given silica oligomers are incorporated into dimers, trimers, cyclic tetramers, etc. in the next observational time increment.

An important property of Markov processes is that they eventually achieve a steady or equilibrium state. At equilibrium, all rows of the transition matrix are the same, meaning that the probabilities of passing from one state to another are independent of the starting state. These rows, called fixed probability vectors, represent the equilibrium proportions of the various states. Mathematically, they correspond to the eigenvector of the transition matrix for which the corresponding eigenvalue is 1.00 (Strang, 1976, p. 192). This means that if the transition matrix is designated as T and the fixed probability vector is designated as v, the following matrix equation holds:

$$Tv = v. \tag{1}$$

To determine the equilibrium state of the transition matrix, the transition matrix must be multiplied by itself, i.e., the matrix must be "powered" a sufficient number of times until stability, as indicated by equality of the rows, is achieved.

If data are available on the aggregate state of the system designated by the vector $\mathbf{a}$ at time t, by the vector $\mathbf{a}_1$ at time t + 1, and by the vector $\mathbf{a}_n$ at t + nδt, where δt is the time increment, the problem is to estimate the transition matrix T from these sequential observations of the aggregate state of the system. The problem of estimating the transition probability matrix from aggregate data vectors, $\mathbf{a}$, $\mathbf{a}_1$, $\mathbf{a}_2$,. . . , $\mathbf{a}_n$, was addressed by Kalbfleisch and Lawless (1984), who used a weighted least-squares method to estimate the individual transition probabilities from sequential observations of the aggregate state. The mathematics of the method of estimation were described in detail by Kalbfleisch and Lawless (1984) and will not be presented here. The basic idea of the procedure is as follows:

$$\begin{aligned} \mathbf{a}_1 &= \mathbf{a} \times T \\ \mathbf{a}_2 &= \mathbf{a}_1 \times T \\ &\vdots \\ \mathbf{a}_n &= \mathbf{a}_{n-1} \times T. \end{aligned} \tag{2}$$

$\mathbf{a}$ is the vector of aggregate data at time t = 0, where T is the transition probability matrix, and $\mathbf{a}_1$ is the aggregate data vector observed after time t = 1, $\mathbf{a}_2$ is the aggregate data vector observed after t = 2, and $\mathbf{a}_n$ is the aggregate data vector at t = n. There are n equations involving the transition probability matrix T, which is estimated from these n equations by weighted least squares (Kalbfleisch and Lawless, 1984).

Once the transition probability matrix T is determined, the equilibrium state of the aggregate k × 1 data vector can be calculated from

$$p = [(t - I)(T - I)' + J]^{-1}(1) \tag{3}$$

where p is the equilibrium state of the aggregate vector, J is a k × k matrix of 1's, I is a k × k identity matrix, and 1 is a k × 1 vector of 1's.

CHEMICAL CONSIDERATIONS

To apply Markov-chain models to silica oligomerization and zeolite crystallization, data are needed for the relative proportions of silica oligomers in solution at some time t. These data can be obtained for concentrated solutions using ^{29}Si NMR (Donahoe and Liou, 1985). Because the process of silica oligomerization is conceptually simple and relatively easy to describe in terms of a Markov-chain model, the oligomerization is discussed in detail below. Modification of the model to include zeolite crystallization is then suggested. This model probably applies only conceptually rather than experimentally to silica oligomerization, because the rates at which different oligomers form and at which the system achieves equilibrium among these species is probably so fast that they cannot be observed experimentally by the NMR method (R. J. Donahoe, University of Alabama, Birmingham, Alabama, personal communication). Zeolite crystallization, on the other hand, is sufficiently slow so that the data needed for the Markov-chain analysis can be gained by the NMR methods of Donahoe and Liou (1985).

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Table 1. Postulated elementary reactions.

Reaction number	Elementary reaction	Rate constant	Rate expression[1]
1	2 M = D + W	k1	k1 $(M)^2$
2	D + W = 2 M	k2	k2 (D) (W)
3	3 M = Tm + 3 W	k3	k3 $(M)^3$
4	Tm + 3 W = 3 M	k4	k4 (Tm) $(W)^3$
5	4 M = Tt + 4 W	k5	k5 $(M)^4$
6	Tt + 4 W = 4 M	k6	k6 (Tt) $(W)^4$
7	5 M = P + 5 W	k7	k7 $(M)^5$
8	P + 5 W = 5 M	k8	k8 (P) $(W)^5$
9	D + M = Tm + W	k9	k9 (D) (M)
10	Tm + W = D + M	k10	k10 (Tm) (W)
11	2 D = Tt + 2W	k11	k11 $(D)^2$
12	Tt + 2 W = 2 D	k12	k12 (Tt) $(W)^2$
13	D + 2 M = Tt + 3 W	k13	k13 (D) $(M)^2$
14	Tt + 3 W = D + 2 M	k14	k14 (Tt) $(W)^3$
15	D + Tm = P + 2 W	k15	k15 (D) (Tm)
16	P + 2W = D + Tm	k16	k16 (P) $(W)^2$
17	2 D + M = P + 3 W	k17	k17 $(D)^2$ (M)
18	P + 3 W = 2 D + M	k18	k18 (P) $(W)^3$
19	D + 3 M = P + 4 W	k19	k19 (D) $(M)^3$
20	P + 4 W = D + 3 M	k20	k20 (P) $(W)^4$
21	Tm + M = Tt + 2 W	k21	k21 (Tm) (M)
22	Tt + 2 W = Tm + M	k22	k22 (Tt) $(W)^2$
23	Tm + 2 M = P + 3 W	k23	k23 (Tm) $(M)^2$
24	P + 3 W = Tm + 2 M	k24	k24 (P) $(W)^3$
25	Tt + M = P + 2 W	k25	k25 (Tt) (M)
26	P + 2 W = Tt + M	k26	k26 (P) $(W)^2$

[1] Rate = k1 $(M)^2$, etc. M = monomer = H_4SiO_4; D = dimer = $H_6Si_2O_7$; Tm = cyclic trimer = $H_6Si_3O_9$; Tt = cyclic tetramer = $H_8Si_4O_{12}$; P = cyclic pentamer = $H_{10}Si_5O_{15}$; W = water = H_2O.

The questions addressed here are: (1) How do the different silica oligomers form? (2) What are the relative rate constants for the pertinent formation reactions? That the oligomers form by collision of monomers to form dimers, trimers, cyclic tetramers, etc. is assumed. The various possible *elementary kinetic reactions* are shown in Table 1. Because these are elementary reactions in the kinetic sense, the rate equations can be written by inspection from the stoichiometry of the different elementary reactions. Furthermore, because of the molecularity of the different elementary reactions, the likelihood of the occurrence of these reactions and, hence, the importance of the elementary reactions to the overall reaction can be estimated. Although numerical values cannot be assigned *a priori* to the rate constants, the various reactions can be ranked in order of importance to the overall rate equation. Furthermore, the various rate constants of the elementary reactions can be recast in the form of equilibrium constants, which can be used to relate the various reactions.

The following criteria were used to judge the importance of the different reactions and associated rate constants: (1) Bimolecular reactions are much more probable than reactions of higher molecularity. (2) Reactions in which the reactants are present at high concentrations are more important than those in which the reactants are present at low concentrations. (3) Monomolecular reactions in which a species decomposes to two other molecules are more likely than those leading to three or more product molecules.

The reactions arranged according to molecularity and concentration of reactants are shown in Table 2. Using these criteria, the following rank order was assigned to

Table 2. Molecularity of reaction vs. concentration of reactants.[1]

Molecularity	Concentration			
	Large	Moderate	Small	Very small
Mono-		2	4, 10	6, 8, 12, 14, 16 18, 20, 22, 24, 26
Bi-	1	9	11, 21, 15, 25	
Ter-	3	13	17, 23	
Quadra-	5	19		
Penta-	7			

[1] Numbers in table refer to reaction numbers in Table 1.

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Table 3. Transition reaction matrix.

From:	To: Monomer	Dimer	Trimer	Tetramer	Pentamer
Monomer	*U*	*k1*[1]	k3, k9	k5, k13, k21	k7, k17, k19, k23, k25
Dimer	*k2*	*U*	*k9*	k11, k13	k15, k17, k19
Trimer	k4, *k10*	*k10*	*U*	k21	k15, k23
Tetramer	k6, k14, k22	k12, k14	*k22*	*U*	k25
Pentamer	k8, k18, k20, k24, k26	k16, k18, k20	k16, k24	*k26*	*U*

[1] Symbols, e.g., k1, refer to rate constants for reactions listed in Table 1. Italicized values indicate dominant reactions according to criteria discussed in text.

the reaction rates for the various elementary reactions of Table 1.

$$1 \gg 2 = 9 > 4, 10, 11, 21, 25 > 15 > 3 > 6, 8, 12, 13, 14, 16, 18, 20, 22, 24 > 17, 23 > 5 > 19 > 7.$$

These reactions were arranged in a form appropriate for a Markov analysis as shown in Table 3. In this table, the rows indicate transitions from a given state to subsequent states as indicated by the columns. Thus, row 1 = "Mon." indicates the transition from the monomeric state to a monomeric state (column 1) or a dimeric state (column 2), trimeric state (column 3), etc. The designation "U" indicates that the state was unchanged by this transition. The designations k1, k3, etc. indicate the rate constants of the reactions shown in Table 1 associated with these transitions. Italicized values are those which, according to the criteria above, are likely to be important reactions. This table summarizes in the form of a transition matrix the important elementary reactions likely to be involved in the oligomerization of silica.

RATE CONSTANTS AND TRANSITION PROBABILITIES

The relation between rate constants and transition probabilities can be shown simply for the familiar first-order reaction of radioactive decay. It is easily shown (see, e.g., Daniels and Alberty, 1966, p. 709) that if 'p' (the probability of disintegration of the nucleus in a time element δt) is independent of the past history of the nucleus, then for a sufficiently short time period, 'p' is proportional to δt, or $p = k\delta t$, where k is a proportionality constant, the decay constant for the reaction. The probability that the nucleus will survive n such intervals is $(1 - kt/n)^n$, where $t = n\delta t$.

For large values of n and small values of δt, the limiting condition is

$$\lim_{n \to \infty} = (1 - kt/n)^n = e^{-kt},$$

which is the integrated form of the first-order reaction for which the rate of the reaction is

$$-dN/dt = kN.$$

Thus, k = the first-order rate constant, and the transition probability is equal to $k\delta t$. Formosinho and Miguel (1979) generalized this approach and extended it to higher-order reactions.

PROPOSED APPLICATIONS

To test the proposed method and to obtain useful information on the mechanism of zeolite formation, Donahoe and Liou's (1985) NMR experiments should be repeated at several different temperatures, and the quantities of the various silica oligomers measured at a number of fixed time increments for each temperature. The resulting data will consist of the quantities of monomer, dimer, trimer, etc. in solution at times $t = 1$, $t = 2, \ldots, t = n$. These results will constitute the aggregate data which can then be used by the method of Kalbfleisch and Lawless (1984) to give n estimates of the transition probabilities for the transition matrix shown in Table 3. Once the transition probabilities are estimated, the rate constants for the various reactions can be calculated as shown by Formosinho and Miguel (1979). This calculation should be straightforward for those rate constants lying adjacent to the main diagonal of the matrix in Table 3. If a transition probability corresponds to an aggregate of reactions, e.g., many of those off the main diagonal of this matrix, transition probabilities may be difficult to decompose into rate constants for the individual reactions. Because of the Markov process and the chemistry of the system, however, a number of constraints can be imposed on the rate constants and transition probabilities. Thus, some of these rate constants can probably be estimated from the composite probabilities by means of linear programming.

The proposed application discussed here is limited to the formation of silica oligomers. The method can be readily extended to the crystallization of zeolites by adding one or more rows and columns to the transition matrix of Table 3. Thus, Table 4 is a matrix for a process in which mainly cyclic tetramers are involved in the formation of a zeolite and in which only a slight probability exists that oligomers will return from the zeolite to the solution phase. These conditions can be seen from the entries in Table 4, in which the probability "tetramer-to-zeolite" is .30, and "zeolite-to-various oligomers" is .0001.

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Table 4. Hypothetical transition matrix.

From:	To: Monomer	Dimer	Trimer	Tetramer	Pentamer	Zeolite
Monomer	.9274	.07	.0025	.00008	.00001	.00001
Dimer	.05	.8395	.10	.01	.0004	.0001
Trimer	.06	.06	.8495	.03	.0004	.0001
Tetramer	.05	.01	.04	.54	.06	.30
Pentamer	.05	.02	.02	.05	.8595	.0005
Zeolite	.0001	.0001	.0001	.0001	.0001	.9995

Table 5. Hypothetical concentrations of silica oligomers and zeolite.

	Monomer	Dimer	Trimer	Tetramer	Pentamer	Zeolite
Time 1[1]	.430	.260	.220	.0600	.0300	.0000
Time 2[2]	.429	.263	.217	.0431	.0296	.0181
Time 3[2]	.428	.265	.214	.0339	.0282	.0311
Time equil.[3]	.0234	.0156	.0110	.00149	.00143	.9473

Time to reach equilibruim[3] = 1500 × δt, where δt = time 2 − time 1.

[1] Assumed initial silica distribution, from Cary *et al.* (1982).

[2] Calculated from Eq. (2).

[3] Calculated from Eq. (3).

The process of modeling zeolite crystallization by this procedure is illustrated in Tables 4 and 5 and is based on the assumed vectors of aggregate data shown in Table 5. Row 1 is the distribution of silica oligomers before onset of zeolite formation, and rows 2 and 3 represent the "observed" silica oligomers and zeolite mass after time increments 1 and 2. The transition probability matrix that converts row 1 to row 2, etc. is that given in Table 4. In actuality, rows 2 and 3 of Table 5 were calculated using row 1 of Table 5, the transition matrix T of Table 4, and Eq. (2). In practice, the rows of Table 5 would be determined experimentally, and the transition matrix T would be calculated by the method of Kalbfleisch and Lawless (1984). Once matrix T has been determined, the equilibrium distribution of the silica oligomers and the zeolite can be obtained from Eq. (3). For the vectors and matrices of this proposed application, the equilibrium vector is shown in row 4 of Table 5. Note that at the equilibrium conditions shown here, the concentration of the silica oligomers is very small, indicating that most of the silica has been converted to zeolite. Note also, that this conversion to zeolite was accomplished mainly through the cyclic tetramer path, with very small additions of the other oligomers directly to the zeolite. Rate constants can be estimated from Tables 3 and 4. From Table 3, the rate constants k1 and k2 can be seen to correspond to transition probabilities .07 and .05 of Table 4. As shown above, $p = k\delta t$, thus, $k = p/\delta t$ for the simple first-order reaction (2). If the actual time increment is known, the numerical values of k can be calculated, although the rate expressions will be more complicated because most of the reactions are not first order. As stated above, Formosinho and Miguel (1979) provided examples of such calculations. Many other possible zeolite-forming reactions involving the gain and loss of the other oligomers by the zeolite structure can be modeled in similar fashion.

SUMMARY AND CONCLUSIONS

One of the very powerful features of a Markov analysis is the ability to predict the equilibrium state of the system. The individual aggregate data for each of the 'n' increments can be used to calculate the equilibrium distribution of the species for the system and, perhaps more importantly, the time required for the system to reach equilibrium. Thus, each observational time increment is δt. The transition matrix can be "powered" until the final equilibrium matrix is obtained, as indicated by the equality of all the rows of the matrix, and no change in value upon further self multiplication. The total time to achieve this state for the experimental conditions is $n\delta t$, where n is the exponent to which the transition matrix must be raised to achieve stability. As shown in Table 5, n = 1500 transitions for the example discussed here.

Because the proposed application of the method would obtain data at several temperatures, the use of the Arrhenius equation should allow rate constants at other temperatures and corresponding equilibrium constants to be estimated. From these data, free energy data on these reactions could be calculated. The precision of the experimental results and numerical procedures used in calculating the equilibrium state and estimating the rate constants will profoundly affect the overall precision of such thermodynamic calculations. Reasonable estimates of parameters for geochemically important reaction mechanisms may thus be obtained that might not be possible otherwise.

Another useful attribute of the Markov chain analysis is that it provides a means to model possible zeolite crystallization mechanisms, as was done in the proposed application discussed above. Here, the transition matrix chosen was a hypothetical one reflecting estimates of the various transition probabilities on the basis of the criteria enumerated above. The starting aggregate data (row 1, Table 5) were the distribution of silica oligomers reported by Carey *et al.* (1982).

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