Dynamics of silicate species in solution studied by mass spectrometry using isotopically labelled compounds

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Figure S1. Possible single corner exchange pathways involving a nonamer intermediate. The first step is insertion of a $^{29}\text{Si}$ atom into a siloxane bond, forming the nonamer. Then either a neighboring siloxane bond needs to be hydrolized and reformed to the $^{28}\text{Si}$ atom before the $^{29}\text{Si}$ is expelled to recreate the octamer (upper pathway) or the $^{29}\text{Si}$ atom replaces the corner via a three-ring intermediate (lower pathway).
Figure S2. Mass spectrum of a solution with the molar composition 1 $^{29}$SiO$_2$ : 1.1 TMAOH : 110 H$_2$O. This is twice the amount of water than in the standard solution of the cubic octamer. As can be seen, a variety of different species is formed.

Figure S3. Development of mass spectra after addition of a solution prepared by hydrolysis of 1 tetramethoxysilane: 1.1 TMAOH : 54 H$_2$O to a solution of the $^{29}$Si octamer. The first solution was added to the octamer solution immediately after the preparation (few seconds) which means that the solution basically contains monomers (ref. 19). From top to bottom 2 min, 50 min, 4.5 h, 22 h. The appearance of $^{28}$Si containing species is substantially delayed compared to the experiment described in Figure 1 of the manuscript. Hydrolysis of tetramethoxysilane is not the delaying factor, since it occurs in less than one minute under these conditions. The majority of the $^{28}$Si containing oligomers appear first at m/z = 555, which corresponds to the concerted exchange of four silicon atoms. The equilibrium distribution is shifted to higher m/z, because there was a slight excess of the octamer solution.
Supporting Methods

Description of the kinetic model for the exchange of faces:
For the development of the model, a statistical distribution of the silicon atoms over the corners of the cubic octamer has been assumed to derive the temporal development of the species. This is not fully correct for the early phases of the exchange, if concerted processes are assumed, since the exchange of faces between a $^{28}$Si cube and a $^{29}$Si cube would lead to one face completely formed from $^{28}$Si atoms and the opposite one from $^{29}$Si atoms instead of a statistical distribution. However, this preferential occupation vanishes after several exchange steps. Since this factor is expected to only moderately influence the modelled distributions, it was neglected in order to keep the model reasonably simple.

If one considers the face of a cube with a certain number of $^{28}$Si atoms replaced by $^{29}$Si atoms one can formulate a probability matrix for finding a certain number of $^{29}$Si atoms on a face in dependence of the total number of $^{29}$Si atoms in the cube:

$$\begin{pmatrix}
70 & 0 & 0 & 0 & 0 \\
35 & 35 & 0 & 0 & 0 \\
15 & 40 & 15 & 0 & 0 \\
5 & 30 & 30 & 5 & 0 \\
1 & 16 & 36 & 16 & 1 \\
0 & 5 & 30 & 30 & 5 \\
0 & 0 & 15 & 40 & 15 \\
0 & 0 & 0 & 35 & 35 \\
0 & 0 & 0 & 0 & 70 \\
\end{pmatrix}$$

The columns represent the probability for a certain number of $^{29}$Si atoms on a face (0 to 4) and the column the number of $^{29}$Si atoms in the cube (0 to 8). One can, for instance, calculate the probability to find two $^{29}$Si atoms on a face for a cube containing four $^{29}$Si atoms as

$$\frac{4 \cdot 3 \cdot 4 \cdot 3}{8 \cdot 7 \cdot 6 \cdot 5} \cdot \binom{4}{2} = \frac{36}{70}$$

The probabilities to find certain numbers of $^{29}$Si atoms in a cube which is formed from two faces of precursor cubes can be obtained from the convolution of the probability distributions calculated from the probability matrix given above. If, for instance, one cube containing three $^{29}$Si atoms reacts with another cube containing four $^{29}$Si atoms, one obtains the probability distribution for the newly formed cube from the convolution of the distributions of the two parent cubes, $\frac{1}{70} (5,30,30,5,0)$ and $\frac{1}{70} (1,16,36,16,1)$ to result in

$$\frac{1}{4900} (5,110,690,1645,1645,690,110,5,0)$$

For the temporal development one has to introduce a reaction probability (rate constant). If $(p_0^i, p_1^i, p_2^i, p_3^i, p_4^i, p_5^i, p_6^i)$ is the probability distribution for the number of $^{29}$Si atoms on the cubes at time $t_1$, one can obtain the probability distribution $(p_0^f, p_1^f, p_2^f, p_3^f, p_4^f, p_5^f, p_6^f)$ at $t_2 = t_1 + \Delta t$ by introducing a rate constant $k$ for the reaction between the cubes and numerical integration of the population balance. A single rate constant is assumed, irrespective of the number of $^{29}$Si atoms in the cubes, since no significant isotope effect is expected for these species.

In the population balance, the probability that a cube with $i$ $^{29}$Si atoms reacts with a cube with $j$ $^{29}$Si atoms is now proportional to $p_i^j \cdot p_j^i$ with the rate constant $k$ as proportionality factor. Thus, the fractions of cubes with $i$ resp. $j$ $^{29}$Si atoms are reduced by $\frac{1}{2} p_i^j \cdot p_j^i \cdot k$, while the gains in the populations of the different cubes can again be calculated by the convolution of the probability functions as described above. This balance is calculated for each time step of the integration for all combinations of $i = 0, \ldots, 8$ and $j = 0, \ldots, 8$.

(The factor $\frac{1}{2}$ enters the equation because two cubes only form one cube in the model incorporating a concerted recombination of one cube by the combination of two faces from the parent cubes while two tetramers are released into the silicate pool. However, this only affects the numerical value of the rate constant by a constant factor of 0.5 which is not relevant for the determination of the activation energies).

By a least mean square method, $k$ is now varied to optimally fit the temporal development of experimental distributions. Similar models were formulated for the exchange of a single silicon atom and two silicon atoms. Formally, the exchange of a single silicon atom between two cubes is identical to a model involving the reaction of a monomeric silicate with a cube, leading to the exchange of one atom.

A similar model can be carried out for the prismatic hexamer. Annotated Mathcad codes for the models are available on request from the authors.