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LOCAL ORDER IN THE DISTRIBUTION OF Si AND Al IN TECTOALUMINOSILICATES

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Local order of Si,Al distribution in tectosilicates is examined under the restriction of both Loewenstein and Dempsey rules. The distribution of various cluster types permissible for a given Si/Al ratio is predicted by the application of the simplex method of linear programming. There is a good agreement between the predicted and observed values.

Precise determination of Si, Al distribution in tectoaluminosilicates including zeolites is very important for understanding not only the topological features of their various networks, but also their charateristic physical and chemical properties. However, it has long been pointed out to be very difficult to distinguish Si atoms from Al atoms in the solid state phase, because their X-ray scattering powers are nearely the same. An alternative approach has been recently introduced by using solid state MAS ^{29}Si NMR for their characterization.[1-3] It gives us the information of nearest neighboring relation between silicon and aluminum atoms in the framework. Many observed data showed clearly the validity of Loewenstein's rule[4] which states that two four coordinated Al atoms can never be nearest neighbors in aluminosilicate structures. Meanwhile, it has also been pointed out that the NMR spectroscopic data could not be completely explained by Loewenstein's rule only, and it would also be necessary to take Dempsey's rule into consideration,[5,8] which states that the number of the second nearest Al neighbors is minimized. Modelling computations under the restrictions of both rules have been tried by Klinowski et al.,[7] Vega,[8] Melchior et al.,[9] Melchior,[10] and Beagley et al.[11] This paper presents a simple mathematical foundation on the problem and a strict solution for it in the case where both rules are stricltly obeyed.

When assuming the validity of Loewenstein's rule, there are only six kinds of clusters (1st coordination network[12]) to be present in the structure (Fig. 1). In this figure, oxygen atoms bridging the cations are omitted.

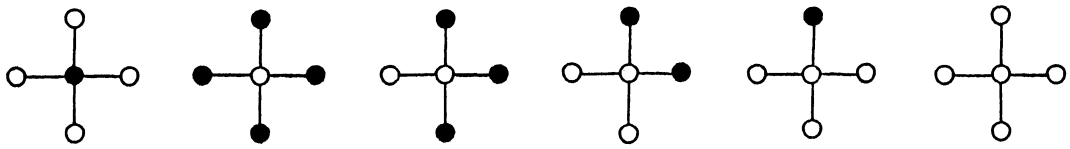

Fig.1. Possible 6 types of clusters, where solid circles are Al and open circles are Si.

Putting Wi as the probability finding a cluster type i, we have the following relations for Wi's and i's, where i=0, 1, 2, 3, and 4 .

$$1/4 \sum_i (4 - i) W_i = W_{Si\text{-}Si} \quad \text{and} \quad 1/4 \sum_i i\, W_i = W_{Si\text{-}Al} \qquad (1)$$

$$\sum_i W_i + W_{0'} = 1 \qquad (2)$$

Here, $W_{Si\text{-}Si}$ and $W_{Si\text{-}Al}$ mean the probabilities of the occurrence of the pairs of Si-Si and Si-Al respectively. Generally speaking, if the values of Wi in the left hand side were given, those in the right hand side could be uniquely determined. However, even if the values in the right hand side were given, those in the left hand side could be or could not be uniquely determined. The former is the case of correlation range s=1 and the latter of correlation range s>1.[13] Correlation range s=1 means that a transition probability from atom A to atom B can be determined by the starting A atom only. In the case of correlation range s>1, there are many different combinations of Wi's in the left hand side of Eq.1 for definite values of W's in the right hand side . Dempsey rule which concerns the second nearest neighbor is obviously in the case of s=2. Apart from further mathematical treatment of s=2, it is possible to solve strictly the cluster values Wi's under the restriction of both Loewenstein and Dempsey rules. The Dempsey rule states that the number of the second nearest neighboring Al-Al is minimized. This is mathematically equivalent that a function defined as $Z= W_2 + 3W_3 + 6W_4$ be minimized under the restriction of Eq.1, where the coefficients of W in the Z function being the number of the second nearest neighboring Al-Al included in each cluster. This is exactly a problem of linear programming and can be easily solved by the simplex method. The result is shown in Fig.2. The abscissa indicates the fraction of Al content defined as X=Al/(Al+Si) or Si/Al, while the ordinate

the fraction of each cluster to be expected. The fraction of type 0' can be obtained by Eq'.2. For example, at X =0.2, type 1(80%) and type 0'(20%), and at X=0.25, type 1(50%), type 2(25%) and type 0'(25%). All of the Si and Al atoms in the tectosilicate network can be qualified to be a center of these clusters. All the structures whose Si and Al positions were precisely determined by X-ray method are examined and compared with this result. They are listed in Table 1. Good agreement is observed between the observed and predicted distribution values except one case of scapolite. One more interesting fact is that the inflection points at Si/Al = 2.0, 1.33 in Fig.2 obviously correspond to the discontinuous points of the unit cell dimensions of faujasite type zeolites as pointed out experimentally by Dempsey.[6] The computational fractions of this work are not strictly consistent with those from Si NMR data of synthetic aluminosilicates.[7,9] This means that, in contrast to the natural silicates, synthetic ones are relaxed in the requirement of Dempsey rule, though still holding for Loewenstein rule. Mathematical treatment for these cases is now undertaken by extending the procedure developed in the present work.

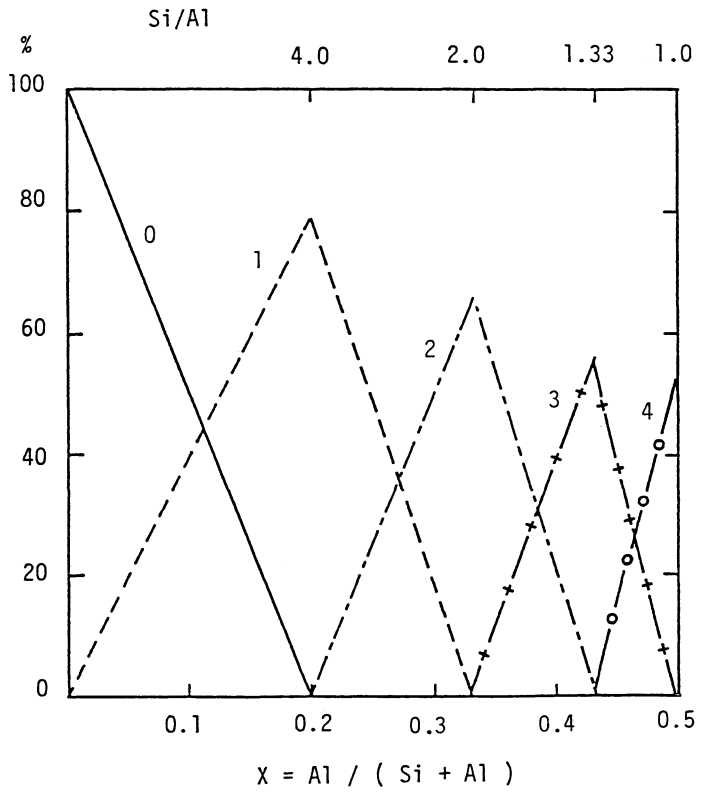

Fig.2. Proportion of cluster types(0, 1,2,3,4) predicted for the various Al contents.

Table 1. Examples of predicted and observed distributions of cluster types (%)

Predicted		Cluster type						
X	Si/Al	4	3	2	1	0	0'	
0.25	3.0	-	-	25.0	50.0	-	25.0	
0.333	2.0	-	-	66.0	-	-	34.0	
0.40	1.5	-	40.0	20.0	-	-	40.0	
0.444	1.25	11.1	44.4	-	-	-	44.4	
0.50	1.0	50.0	-	-	-	-	50.0	
Observed								silicate species
0.25	3.0	-	-	25.0	50.0	-	25.0	albite
0.25	3.0	-	-	25.0	50.0	-	25.0	yugawaralite
0.333	2.0	-	-	66.0	-	-	34.0	laumontite
0.333	2.0	-	33.3	-	33.3	-	33.3	scapolite
0.40	1.5	-	40.0	20.0	-	-	40.0	edingtonite
0.444	1.25	11.1	44.4	-	-	-	44.4	cordierite
0.50	1.0	50.0	-	-	-	-	50.0	zeolite A, gismondite

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