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Framework and Non-Framework Cation Ordering Phenomena

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The interplay between short- and long-range interactions leads to interesting phenomena, both with zeolite constituents as well as with those researching them. In considering over a decade of interactions with Prof. Takaishi and his work, on the occasion of his 77th birthday, it is the number of overlaps in the paths that our separate research interests have followed that is perhaps most notable. It is a privilege to have the opportunity to recount some of these overlaps in a personal fashion and, in so doing, to express my respect for Prof. Takaishi and my appreciation for the many fruitful ideas he has already contributed; I am certain there will be many more.

Keywords: Aluminum distributions, Si-29 NMR, gallosilicates, non-framework cations, structure design, molecular simulation

Although indirect overlaps came earlier, as noted beneath, my first direct, yet still long range interaction with Prof. Takaishi occurred in 1987, immediately following his analysis of aluminum distributions in zeolite omega¹⁾. Having just completed a structural study of the MAZ-framework gallosilicate analog of zeolite omega²⁾, we had scrutinized also aluminosilicate^{3,4)} and gallosilicate⁵⁾ LTL-framework materials using powder neutron diffraction. Of particular interest were the distributions of the framework cations. While ²⁹Si NMR had already yielded detailed information on the local orderings of aluminum and gallium in FAU-framework materials such as zeolite X and Y and their gallosilicate counterparts⁶⁾, these structures have but a single unique T-site (T = Tetrahedral species, Si or Al). Zeolite omega (MAZ-framework) and L (LTL - Fig.1) possess two, with average local environments that are similar in L, but quite different in omega. Thus, for example, the Si-2Al band positions in the ²⁹Si NMR spectrum

of L overlap closely, while those in omega are offset from each other by several ppm. The diffraction data on the LTL-framework materials provided information on the partitioning of aluminum³⁾ or gallium⁵⁾ over the two inequivalent T-sites together with good geometrical data. We then applied a profile analysis method, already well established for analysis of powder diffraction data, to the ²⁹Si NMR spectrum⁷⁾ to help interpretation of the details. The peak positions for both zeolite omega and zeolite L, computed on the basis of our analyses of the geometrical⁸⁾ and compositional⁹⁾ dependencies of the ²⁹Si chemical shifts agreed encouragingly well with experiment¹⁰⁾.

We were, to some degree, satisfied, but Prof. Takaishi was immediately interested in extracting still more from the data. At his direct instigation, we applied profile analysis to the ²⁹Si NMR spectrum of gallosilicate zeolite L. We did not, though, estimate Si-*n*Ga peak positions as the data on the compositional dependence of the ²⁹Si chemical shifts in FAU-framework gallosilicates, the basis for quantifying the deshielding influence of first and second neighbor gallium atoms, was

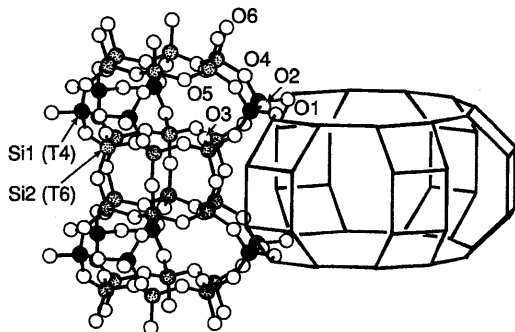


Fig. 1 The LTL-framework structure drawn so as to illustrate the lobe in the one-dimensional 12-ring channels (right), the two crystallographically inequivalent T-sites and the accepted numbering of the framework constituents (after 4).

much sparser (Fig.2). Armed with the aluminosilicate and gallosilicate data, Prof. Takaishi developed a detailed analysis of the local aluminum and gallium orderings that reproduced well the experimental Si- n Al and Si- n Ga intensities¹¹⁾. He also used similar methods to consider aluminum distributions in mordenite¹²⁾, in zeolite X¹³⁾, in analcimes¹⁴⁾, in ZK-19 and chabazite¹⁵⁾, some of which results were highlighted in this same publication¹⁶⁾, and in mordenite¹²⁾. In the lattermost study Prof. Takaishi proposed a limiting composition of Si₄Al for 5-ring units.

The drivers of measured aluminum distributions have been very intensively studied. Loewenstein's rule of Al-O-Al linkage avoidance was known to be followed invariably in Si:Al > 1 materials produced by hydrothermal crystallization. The role of 'Dempsey's rule' of Al-O-Si-O-Al second neighbor avoidance was less clear, and the analysis of Takaishi et al. of mordenite indicated it to be inconsequential¹⁷⁾. Here, again, our interests intertwined, but from quite different directions. Rather than detailed analyses of combinations of local configurations, in our work we leveraged the burgeoning power of direct computer simulation. We explored how Loewenstein's rule and Dempsey's rule would be manifested in aluminum distributions in LTA and FAU-framework zeolites as a function

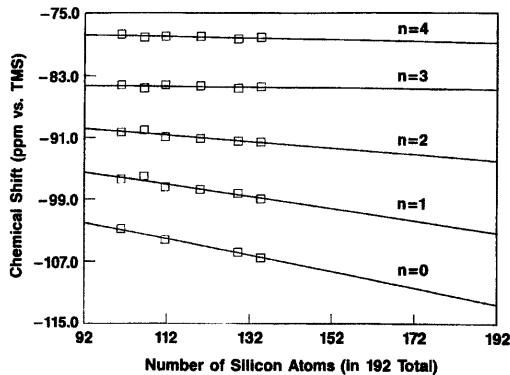


Fig. 2 The quantitative deshielding influence of second-neighbor gallium atoms can be extracted from the distinct variations in the ²⁹Si chemical shift of silicon atoms with 0, 1, 2, 3 and 4 first neighbor gallium atoms, in FAU-framework gallosilicates (for more complete data on aluminosilicates see 9).

of Si:Al ratio. Taking periodic models of the actual framework topologies, an extension of precursor work based on cubic and diamond lattices¹⁸⁾, we used simulated annealing to optimize aluminum distributions subject to variably weighted first and second neighbor avoidance^{19,20)}.

As would be predicted from Prof. Takaishi's analyses of local orderings, the experimental Si- n Al populations could not be reproduced satisfactorily by these random simulations¹⁹⁾. The aluminum distributions in zeolites of type X are more ordered that would be developed solely through application of Loewenstein's and Dempsey's rules. Prof. Takaishi explored the concept that the details of a zeolite material might, in fact, convey insight into certain of the molecular controls at synthesis²¹⁾, a concept also developed in Melchior's detailed analysis of aluminum distributions in FAU-framework materials^{22, 23)}.

Aluminum distributions warrant scrutiny, given the significant impact they have on intrinsic properties. Prof. Takaishi, for example, has considered the acidity in zeolite L²⁴⁾ and the distribution of non-framework cations in systems such as sodium zeolite A²⁵⁾ and analcimes¹⁴⁾.

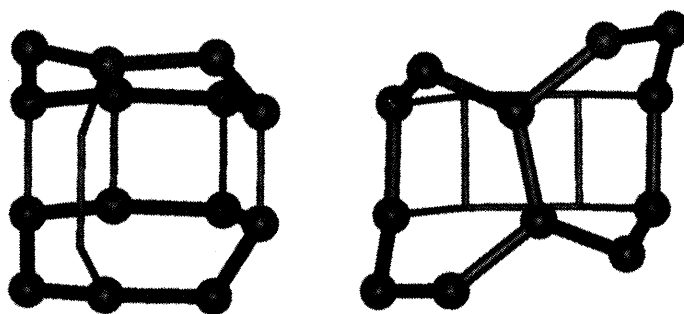


Fig. 3 Two cages suitable for constructing zeolite frameworks, drawn as interconnected T-atom nodes, both of which have two 7-member rings (highlighted with spheres) and face symbols $4^2 4^1 7^2 8^n$ ($n=1$ left, $n=2$ right). The *kqd* cage (left) has been described by J.V.Smith in his compilation of polyhedra and cages (J.V.Smith, private communication 1994). The cage at right has not, to the best of the author's knowledge, been categorized previously and, having a 77 motif, is offered here as the "Takaishi cage".

The latter framework type represents another overlap point, having been the subject of crystallographic studies²⁶⁾. A particularly interesting case is sodium zeolite X, given its complexity, the role of non-framework cation placement in determining properties, and the data available on crystallographic structures and on aluminum distributions. Prof. Takaishi considered which sites would be the most favorable for non-framework sodium cations given assumed local aluminum distributions. For sodium zeolite X he obtained good agreement with the averaged diffraction results²⁷⁾. Our related path in this area, beyond adding to accumulated crystallographic knowledge, was to develop simulation protocols that would be able to automate, reliably, this prediction of non-framework cation configuration. Applied first to zeolites Li-A(BW)²⁸⁾ and A^{28,29)}, then also to zeolite X³⁰⁾, the methodology has been improved substantially³¹⁾ and appears to have broad applicability. It may indeed provide a useful vehicle, sought by Prof. Takaishi, for relating measured non-framework configurations to framework cation distributions.

Short range interactions had opportunity to operate in 1990, at the time of the "Chemistry of Microporous Crystal Meeting" in Tokyo, when I finally had the opportunity to meet Prof. Takaishi in person and to enjoy both scientific and social

discussions. The latter, I well recall, continued over several hours and locales.

Our overlaps predate, though, the first communications and meetings. Our recent consideration, analytically and by simulation, of the effect of varying concentrations of pore-blockage in 1-, 2- and 3-D pore systems^{32, 33)}, steps firmly in the footprints left earlier by Prof. Takaishi who, some 20 years ago now, applied percolation theory to zeolite A with varying degrees of calcium substitution for sodium³⁴⁾ and potassium³⁵⁾. A long-standing interest in developing methods to simulate the behavior of sorbates within microporous crystals³⁶⁾, resonates with Prof. Takaishi's recent considerations of the influence of local environment on the clustering of dioxygen molecules^{37,38)}. With an analysis of possible polyhedral constituents of zeolite frameworks (Fig.3), simulation also provides a route to virtual libraries of zeolite structures.

While never having had the opportunity to be a formal collaborator, these many overlaps evidence that my own research interests have followed closely those of Prof. Takaishi. Based on this close alignment of interests over the past decade or so, I can only guess that Prof. Takaishi is now intrigued by the application of combinatorial and high throughput experimentation techniques^{39,40)}

to opportunities in zeolite science and application. I look forward to stimulating discussions with him on this topic, an appropriately expansive one with which to start the next millennium.

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