

## O triclusters revisited: Classical MD and quantum cluster results for glasses of composition (Al<sub>2</sub>O<sub>3</sub>)<sub>2</sub>(SiO<sub>2</sub>)

J. A. TOSSELL<sup>1</sup> AND J. HORBACH<sup>2</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, Univ. of  
Maryland, College Park, MD 20742, USA  
(tossell@chem.umd.edu)

<sup>2</sup>Institut für Physik, Johannes Gutenberg-Universität,  
Staudinger Weg 7, D-55099 Mainz, Germany  
(horbach@uni-mainz.de)

The <sup>17</sup>O NMR spectrum of CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> glass shows two types of O sites which are not present in the crystalline material. One of these, with <sup>17</sup>O NMR parameters C<sub>Q</sub> = 2.3 MHz and δ = +20 ppm, was assigned to a "tricluster" O, a local geometry in which the O is coordinated to three tetrahedrally coordinated atoms, either Al or Si. However, several different quantum chemical cluster calculations employing energy-optimized geometries for various tricluster species have given C<sub>Q</sub> values considerably larger than that seen experimentally in the CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> glass. We have recently shown that for edge-sharing geometries, in which the tricluster O atoms participate in "two-membered rings" of composition Al<sub>2</sub>O<sub>2</sub>, the calculated C<sub>Q</sub> values are considerably lower, in the range identified in the glass. A recent classical MD simulation of the structure of glassy aluminum silicate AS<sub>2</sub>, (Al<sub>2</sub>O<sub>3</sub>)<sub>2</sub>(SiO<sub>2</sub>) gave a predominance of O triclusters within 2-membered rings. We have now calculated <sup>17</sup>O nuclear quadrupole coupling constants and NMR shielding values for clusters extracted from these simulations. The calculated C<sub>Q</sub> values for these O triclusters are now in the range observed experimentally in the CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> glass (around 2.3 - 2.6 MHz) when the tricluster O is surrounded by three Al, two of which are part of an Al<sub>2</sub>O<sub>2</sub> ring.

## Molecular orbital study on dissolution of allophane with dilute alkali solution

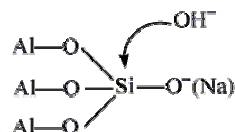
Z. ABIDIN, N. MATSUE AND T. HENMI

Faculty of Agriculture, Ehime University, 3-5-7 Tarumi,  
Matsuyama 790-8566 Japan

Allophane is a hydrous aluminum silicate of hollow spherical morphology with some pores, and wall of the sphere is composed of gibbsite sheet with orthosilicate attached to inside of it. Allophane is known to be susceptible to alkaline condition than layer silicates, but detailed dissolution mechanism has not been known. Here we present molecular orbital calculation results for the interaction between allophane and dilute alkali solution, with focusing nucleophilic attack of hydroxyl ion on Si atom exposed at the pore region of allophane.

Model cluster of allophane simulated the pore region, in which each Si atom is attached to gibbsite sheet via three Si-O-Al bondings with one Si-OH exposed. Molecular orbital calculation was done with semiempirical MOPAC-PM3 and AM1 method in WinMOPAC program (ver. 3.9, Fujitsu).

We assumed that the hydroxyl ion first attacked Si atom at the pore, and formed five-coordinated Si as an intermediate product. The nucleophilic attack of hydroxyl ion was indicated to be promoted by adsorption of Na<sup>+</sup> which added as NaOH, because calculated positive charge of Si atom was greater for Si-O-Na than for Si-O<sup>-</sup>. Si-O bond length was also greater for the Na<sup>+</sup> exchanged model.



By forming five-coordinated Si, bond order of not only the original four Si-O bondings, but adjacent Al-O and O-Al inside bondings also decreased. This suggests that one Si atom dissolution may be followed by three Al atoms dissolution, and is in good agreement with our previous experimental results carried out at about pH 12.

Molecular orbital calculation was also done with some water molecules added around Na<sup>+</sup> to simulate reactions in water, but the obtained result was similar to that in vacuo.

The overall reaction of allophane dissolution with dilute NaOH solution is proposed as: fast cation exchange reaction to produce Si-ONa, followed by nucleophilic attack of hydroxyl ion on Si atom of increased positive charge, then dissolution of Si and Al through bond weakening.