

Isotopic and chemical characteristics of precipitations in recent years in Niigata Prefecture, Japan

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In order to investigate (i) the characteristics of precipitations in Niigata Prefecture in recent years, and (ii) the sources of precipitations in Niigata Prefecture, oxygen stable isotopic ratios (i.e., $\delta^{18}\text{O}$) and the concentrations of major ions were measured. Precipitation samples were collected in polyethylene bottles and filtered using a 0.8 μm Millipore filter at the rooftop of Niigata University after rainfall events. Moreover, precipitation samples from 9 spots in Niigata Prefecture were supplied by Niigata Prefectural Research Laboratory for Health and Environment.

Oxygen stable isotopic measurements were performed by stable isotope ratio mass spectrometer (Micromass PRISM), and major ions were determined by ion chromatography (Cl^- , NO_3^- , SO_4^{2-}), by atomic absorption spectrophotometer (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), by indophenol blue absorption photometry using spectrophotometer (NH_4^+), and by pH meter (H^+).

Consequently, the following matters have been clarified for the precipitations in Niigata Prefecture in recent years. (1) The mean $\delta^{18}\text{O}$ value of precipitation was -9‰ , and the variation of $\pm 7\text{‰}$ was shown throughout the year. (2) All of 9 observation points, the seasonal behavior of isotopic ratio was similar to each other, and the variation of $\delta^{18}\text{O}$ in winter was smaller than that in the other seasons. (3) In June and January, $\delta^{18}\text{O}$ values of precipitation was small, and was large in August. (4) In January, the relationship between the temperature of observation points and $\delta^{18}\text{O}$ values in precipitation was most remarkably found throughout the year. (5) It was proven that the concentrations of Ca^{2+} , SO_4^{2-} and NO_3^- strongly affect on pH by applying the multiple regression analysis to the data obtained. (6) The concentrations of Na^+ , Mg^{2+} , Cl^- increase in winter by sea salt that was brought with the northwestern winter monsoon. (7) It is considered that pH and the concentration of nss-Ca^{2+} increase with the yellow wind from Eurasian Continent in spring.

References

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Interaction of two $\text{Si}(\text{OH})_4$ monomers: An ab initio molecular orbital study

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Molecular orbital modeling of silicate clusters can be used to understand the basic nature of glass structure. Here we studied the structural and energy changes of two $\text{Si}(\text{OH})_4$ monomers with variable intermonomer distances.

For the present ab initio molecular orbital calculations, HF/3-21G*, HF/6-31G(d,p), HF/6-31+G(d,p) and B3LYP/6-31+G(d,p) chemical model/basis set combinations were used. Reported values below are from B3LYP/6-31+G(d,p) calculations. During geometry optimization, all structural parameters except Si-Si distance were allowed to change. At certain distances, full geometry optimizations were performed to obtain stable structures. In order to confirm stability of the structures, vibrational calculations were also done (HF calculation only).

When the Si-Si distance is reduced from initial 8 Å, the total energy lowered significantly as hydrogen bond forms. The stable configuration was found at the Si-Si distance of 4.66 Å. In the fully optimized structure, two hydrogen bonds (2HB) were observed between the monomers with hydrogen bond distance of 1.81 Å. It was the lowest energy configuration in this system. When the Si-Si distance is reduced further, the energy of 2HB form increased rapidly, and then a structure with three hydrogen bonds (3HB) form emerged. The fully optimized 3HB form has the Si-Si distance of 4.13 Å. Hydrogen bond distances of the form are 1.92, 2.01 and 2.20 Å. Beyond this 3HB, we observed four hydrogen bonds (4HB) configuration at the Si-Si distance of 3.87 Å. Hydrogen bond distances for the form are 2.16 (x2) and 2.28 Å (x2). These forms can be used to study the hydrogen bond in the silicate glasses.

When the distance was further reduced (< 3.0 Å), new Si-O bonds began to form between the $\text{Si}(\text{OH})_4$ monomers, resulting penta-coordinated silicons. The stable structure is an edge-shared penta-coordinated dimers, in which each shared oxygen is coordinated by two penta-coordinated silicons and one hydrogen. This structure is interesting, because this local structure resembles to an observed "defect complex" for diffusion in molecular dynamics simulation of BeF_2 melt (Brawer, 1984). Therefore, this penta-coordinated dimer would be very useful to model the diffusion process of fully polymerized melt and the formation of high coordinated Si under pressure.

References

Brawer, S.A., (1984), in *Point Defects in Minerals*, p.36, edited by Schock, R.N., AGU.