

Formation of hydrated-alumina clusters toward elucidation of chemical processes on mineral surfaces

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Small particles consisting of ice, minerals, and organic molecules exist in the early stage of planetary formation. It is a prevalent hypothesis that, in protoplanetary nebulae, organic molecules are formed through catalytic reactions on mineral particles. To investigate essential reaction steps of the organic-molecule formation, size-selected clusters of mineral composition can be used as models for chemistry on mineral surfaces. As a first step, we investigated generation of mineral-composition clusters by focusing on compounds of aluminum, whose elemental abundance is relatively high in the earth and in space.

Aluminum is known as a reactive metal as we can imagine from the fact that it is readily oxidized by O₂ and/or H₂O in the air to form a passive surface. We have reported that aluminum-cluster cations, Al_N⁺, react with a H₂O molecule to form Al_NO⁺, which implies H₂ generation [1]. In the present study, we investigated reaction of Al_N⁺ with a mixture of O₂ and H₂O gases to observe formation of clusters with composition of aluminum minerals abundant naturally.

In the experiment, Al_N⁺ ($N = 1-14$) were generated by a magnetron-sputter cluster-ion source. They were mass-selected and guided into a reaction cell filled with a buffer He gas containing H₂O and O₂. The ions produced by the reaction of Al_N⁺ with H₂O and O₂ were identified by a quadrupole mass analyzer.

Reaction products with a mass of 157 and 175 amu were observed for all the sizes except $N = 1$. Since only Al⁺ was found to be inert, we speculated that these products originate from Al₂⁺, which is produced by dissociation of Al_N⁺ ($N \geq 3$). By controlling the partial pressures of O₂ and H₂O, reaction intermediates such as Al₂O⁺, Al₂O₃⁺, Al₂O₄H₃⁺, and Al₂O₅H₅⁺ were observed, and the prominent products were assigned to be Al₂O₆H₇⁺ and Al₂O₇H₉⁺ for 157 and 175 amu, respectively. The chemical composition of these products, Al₂O₃(H₂O)_{*n*}H⁺, is similar to that of hydrated alumina such as boehmite, diaspore, and gibbsite except for the excess proton. To obtain structural information of these products, we performed collision-induced dissociation experiment of Al₂O₆H₇⁺ (157 amu) with an Ar gas, where products of 139 and 121 amu were observed. The prominent product of 157 amu was thus identified as Al₂O₄H₃(H₂O)₂⁺ with two H₂O molecules remaining intact.

We further investigated formation processes of these protonated hydrated-alumina clusters by observing the reaction steps to model reactions of aluminum in natural environments; each reaction intermediate was generated in the cluster source, and reaction with either H₂O or O₂ was examined in a step-by-step manner. It was found that reaction of aluminum with O₂ and H₂O to form alumina, Al₂O₃, at initial steps is followed by successive hydroxylation and hydration reactions.

References

- [1] M. Arakawa, K. Kohara, and A. Terasaki, 2013, *Eur. Phys. J. D* 67, 80.