The effect of clathrate formation on concentrations of ammonia and ammonium ion in a subsurface ocean of Enceladus

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The Saturn's icy moon Enceladus could have a global subsurface ocean beneath the icy shell. Cassini spacecraft has found water plumes near the south pole and investigated those components. The Cassini INMS (Ion and Neutral Mass Spectrometer) data showed that the plume includes H_2O, CH_4, CO_2, NH_3, and many other organic materials. Basically, these components reflect those of subsurface ocean but it might be affected by clathrate formation in the ocean and its decomposition process through the pluming activity. Clathrate hydrates are crystalline inclusion compounds, in which hydrogen-bonded water molecules form cages containing hydrophobic gases called guest molecules. Bouquet et al. (2015) suggests that clathrate hydrate should be stable in the icy shell deeper than 22 km in Enceladus. To understand the chemical environment of the subsurface ocean, we need to evaluate the effect of clathrate formation on chemical concentrations in the seawater and/or the plume. We considered an inclusion of ammonium ion into clathrate hydrate. Cassini INMS data showed that a mixing ratio of ammonia in the plume is 0.8%. Ammonia does not form clathrate hydrate, while ammonium ion can be replaced with a part of water cages of clathrate hydrate. The inclusion of ammonium ion into clathrate hydrate could affect the concentration of ammonium ion in the subsurface ocean, therefore, we experimentally investigated the amount of ammonium ions that can be included into clathrate hydrate and evaluated the concentration of ammonium ions and ammonia in Enceladus's subsurface ocean.
Clathrate hydrate was crystallized in the ammonium salts solution and the concentration of ammonium ion in the hydrate and that in the residual solution were measured. As a guest molecule of clathrate hydrate, we used tetrahydrofuran (THF) as an analogue for CH_4 and CO_2. And we used ammonium chloride as an ammonium salts because chloride has been detected in the Enceladus plume. Finally, we measured the concentration of ammonium ion in THF hydrate (C_s) and the concentration of ammonium ion in residual solution (C_L) and determined the partition coefficient, the ratio of C_s to C_L ($K_D=C_s/C_L$). From the partition coefficient and the ammonia concentration observed by Cassini, we calculated a change of concentration of ammonium ion in the plume with time and estimated a possible range of concentration of ammonium ion and that of ammonia in the present subsurface ocean.

Keywords: Enceladus, clathrate hydrate, ammonia, ammonium ion

