

## Ion hydration and contact ion pair structure in supercritical water: X-ray absorption fine structure and molecular dynamics studies

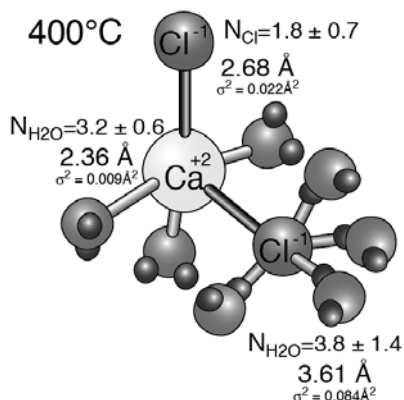
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Ion-water and ion-ion interactions underlie processes in nearly all aqueous systems. In liquid systems they are the basis of many biochemical functions and methods for ion exchange separations. At temperatures near and above the critical point of water, ion pairing dominates certain types of transport in the earth's crust and it is an ever-increasing component of industrial processes from power plant water chemistry to chemical synthesis.

X-ray absorption fine structure (XAFS) spectroscopy, coupled with molecular dynamics (MD-XAFS) are used to test and refine structural models of these systems. As an example [1], a clearer picture of hydration of common ions such as  $\text{Cl}^-$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  has emerged from XAFS that allows one to measure the structure in the first solvation shell about ions including precise measurements of the atomic distances, coordination numbers and oxidation states.

High-temperature XAFS methods for lighter elements are described and results of EXAF and XANES analysis at the Cl and Ca K-edge are reported. The structure of  $\text{Ca}^{2+}/\text{Cl}^-$  ion pairs at 400°C is reported [2]. The coordination structure of various transition metal ions such as  $\text{Mn}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Ag}^+$ , with halides will be described.



**Figure 1:** Schematic of the  $\text{Ca}^{2+}/\text{Cl}^-$  ion pair at 400°C.

[1] Dang, L. X., Schenter, G. K., Glezakou, V. A. & Fulton, J. L. (2006) *J. Phys. Chem. B* **110**, 23644. [2] Fulton, J. L., Chen, Y., Heald, S. M. & Balasubramanian, M. (2006), *J. Chem. Phys.* **125**, 094507.

## Impact synthesis of organic compounds: Implication for their mass production on the early Earth

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How to prepare prebiotic organic molecules on the early Earth has been debated vigorously. One of points of debates is how to overcome the difficulty to produce prebiotic organic molecules under moderately oxidizing  $\text{CO}_2$  and  $\text{N}_2$ -rich early atmosphere [1]. Previous investigators suggested the existence of early oceans well before 4.0 Ga, late heavy bombardments at around 4.0 Ga and the earliest life at 3.8 Ga. In order to connect these geological evidences, we hypothesized that meteorite impacts, which brought many reductants, on the early oceans followed by interaction with the atmosphere was responsible for production of prebiotic organic molecules [2, 3].

In order to simulate the impact reaction, we performed shock-recovery experiments with single-stage propellant gun. The shocked materials are composed of mixture of iron, nickel, carbon, water and gaseous nitrogen or dissolved ammonia. The carbon in the starting materials is enriched in 99% of  $^{13}\text{C}$  so that the C-bearing products can be distinguished from contaminants. These mixtures were encapsulated in metal containers and then shocked with impact velocities of 1 km/s.

Analyses of the experimental products were performed using the state-of-the-art LC/MS and GC/MS. Various organic molecules are detected and some are found to be composed only of  $^{13}\text{C}$ , suggesting syngenetic formation of organic molecules during the shock experiments. This result further suggests that the late heavy bombardment on the early oceans triggered to form a large mass and variety of prebiotic organic molecules on the early Earth.

[1] Ohmoto *et al.* (2006) *Nature* **442**, 908–911. [2] Nakazawa, H., Origin of Life Scenario Written by the Earth (in Japanese), Shin-Nihon Shuppan Ltd., Tokyo (2006). [3] Furukawa Y. *et al.* (2007) *Earth Planet. Sci. Lett.* **258**, 543–549.