Isotope effect in the formation of solid water by surface reactions at 10 K

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D/H ratio of water in molecular clouds (MCs) is often 2-3 orders of magnitude higher than that of terrestrial ocean water ($D/H \sim 1.56 \times 10^{-4}$). Such a significant deuterium enrichment often observed not only for water but also organic compounds like formaldehyde and methanol in MCs [1] cannot be explained by the gas-phase fractionation only. It is at present widely recognized that grain-surface reactions are crucial for the formation and deuterium enrichment of those molecules.

Among various reactions proposed, the reaction $OH+H_2 \rightarrow H_2O+H$ is considered to have a significant contribution (>70%) to H_2O formation in dense MCs [2] where the typical temperature is ~10 K. It is therefore reasonable to assume that deuterated water like HDO could also be formed by the similar surface reactions such as $OH+D_2 \rightarrow HDO+D$ and $OD+H_2 \rightarrow HDO+H$. In the present study, we performed laboratory experiments on the formation of water (H_2O, HDO, or D_2O) by reactions of OH/OD with H_2/HD/D_2 on a solid substrate at 10 K.

Experiments were performed under ultra-high vacuum conditions (~10^{-8} Pa). OH or OD radicals were produced by the dissociation of H_2O or D_2O in microwave-induced plasma and coolded to 100 K. Each radical was codeposited with H_2, HD, or D_2 on a substrate at 10 K.

We found that all reactions studied occur on the substrate at 10 K. However, the reaction efficiency was clearly different between H- and D-atom abstraction reactions from H_2 , HD, or D_2. The former reactions (e.g. $OH+H_2 \rightarrow H_2O+H$) were about 10 times more efficient than the latter (e.g. $OH+D_2 \rightarrow HDO+D$). The difference in efficiency is derived from the different effective masses of reactions. The efficiency does not depend on the kind of hydroxyls (OH or OD) but only on that of atoms abstracted.

The present study suggests that one of the important factor to control the D/H ratio of water in MCs is OD/OH ratio. If OD and OH were produced by D- and H-addition to O atoms on grains, respectively, atomic D/H ratio in MCs would be crucial for constraining the D/H of water in MCs.

[1] Roueff & Gerin (2003) *Space Sci. Rev.*, **106**, 61–72. [2] Cuppen & Herbst (2007) *Astrophys. J.*, **668**, 294–309.

Distribution of iron (II) in the Northwestern Pacific

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Iron is an essential micronutrient for marine phytoplankton and its availability affects marine primary production in the ocean. Among iron species in seawater, Fe(II) is readily bioavailable form for phytoplankton, but its distribution is not clearly revealed. In this study, the distribution of Fe(II) along the 160° E line in the Northwestern Pacific was investigated. Seawater samples were collected during the R/V Hakuho-maru cruise (6 July – 3 August, 2012) with acid cleaned X-Type Niskin samplers deployed onto a CTD-CMS. Dissolved Fe(II) was determined quickly after sampling onboard the ship with luminol chemiluminescence method [1].

We observed the Fe(II) maximum (6 – 54 pM) in the oxygen minimum zone (OMZ) commonly. Dissolved oxygen concentrations were 14 - 58 μM in the OMZ, where in-situ Fe(III) reduction did not occur. During the remineralization process of biogenic particles, Fe(II) was probably released and / or produced in the reducing conditions within the settling particles [2].

[1] King *et al.* (1995) *EST* 29, 818-824. [2] Kondo & Moffett (2013) *DSR-I* 73, 73-83.

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