

Experimental study of the effect of pH on mercury isotopic fractionation during photoreduction

K. NAKABAYASHI, S. SAKATA, T. OHNO

Dept. of Chemistry, Gakushuin Univ., Japan,
(18142022@gakushuin.ac.jp)

Mercury is one of the most concerned toxic heavy metals. Because of the bioaccumulation effect, the concentration of mercury in fish increases in the marine food web. In mercury isotopes of natural biogeochemical samples, both mass dependent and independent fractionation (MDF and MIF) are observed. Previous studies demonstrated that MDF in mercury isotopic composition was caused by chemical reactions such as bacterial reduction, abiotic oxidation, etc. On the other hand, MIF was derived from specific reactions such as photoreduction of mercury by UV ray and its liquid-vapor equilibrium.⁽¹⁾ Recent experimental studies suggested that the MIF observed in the natural biogeochemical samples were related to two mechanisms; Magnetic Isotope Effect (MIE) and Nuclear Volume Effect (NVE).^{(1), (2)} In this study, we focused on the relationship between pH of reactor solution and MIF of Hg isotopes through its photoreduction and vaporization.

We used handy UV lamps for photoreduction. The UV wavelength of 365 nm was used. We performed experiments with both basic and acidic conditions by adding HCl and NaOH. The solution containing organic matters was prepared by dissolving of approximately 3 ng/ml of humic acid. The concentration of Hg solutions was determined by ICP-MS, after that, Hg isotopic ratios were measured by Cold Vapor-MC-ICP-MS.

Under the acidic and basic conditions, negative and positive MIF were observed, respectively. In our expectation, this is caused by the difference of mercury complexes between two conditions; however, further investigation is required to verify this hypothesis. We also compared the variation of MIF with/without humic acid. For each liquid condition, the experiments with humic acid exhibited in much faster reduction rate of Hg²⁺. This result indicates that dissolved organic matter triggered the higher radical reaction. However, the degree of MIF in the solution with humic acid was almost identical to that in the solution without humic acid. In this presentation, we would like to discuss the possible mechanism of MIF.

(1) B. A. Bergquist and J. D. Blum, *Science*, **318**, 417, (2007)

(2) N. Estrade et al., *Geochim. Cosmochim. Acta.*, **73**, 2693, (2009)