Pre-concentration of mercury from low concentration samples for isotopic analysis

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Mercury is a toxic heavy metal that biomagnifies in aquatic food webs. Because Hg can exhibit both Mass-Dependent (MDF) and Mass-Independent Fractionation (MIF), Hg isotopes are providing valuable information for tracing pathways and sources of Hg, and specific chemical pathways, such as photochemical reduction [1]. However, it is still challenging to analyze Hg isotopic compositions in the low concentration samples such as plankton and seaweed which can cause the primary accumulation of Hg from the seawater. In this study, we developed a new pre-concentration method by Chelex-100 from low concentration samples for Hg isotopic analysis and investigated the degree of isotopic fractionation during the pre-concentration.

Mercury was separated from other elements in a sample by using Chelex-100 chelating ion-exchange resin, which has functional iminodiacetic acid (IDA) groups in a styrene-divinylbenzene matrix. Firstly, the sample solution was introduced to a column with a condition of pH = 5. Subsequently, Hg was eluted by 6M HCl. Finally, the concentration of the resultant Hg solutions was determined by ICP-MS, and Hg isotopic ratios were measured by Cold Vapor-MC-ICP-MS. Furthermore, the matrix effect was evaluated by comparing the response of Hg isotopes in 1.0 M HCl to those in 0.1, 0.5, and 2.0 M HCl, respectively.

The sample in 0.5 M HCl showed no significant isotope fractionation compared to that in 1.0 M HCl. We obtained the value of δ^{202}Hg of -0.34 ± 0.15‰ and 0.2 ± 0.4‰ when the sample solutions were adjusted to 2.0 and 0.1 M HCl, respectively. Consequently, the sample solutions should be adjusted to 0.5-1.0 M HCl to reduce the acid matrix effect when measuring Hg isotopic ratios. The recovery of the pre-concentration protocol was >95% in the final Hg eluates. The δ^{202} and Δ^{199} values for Hg reference solution processed by the pre-concentration protocol were 0.09 ± 0.12 ‰ and -0.01 ± 0.03 ‰, suggesting no isotopic fractionation during the pre-concentration. In conclusion, the present study demonstrated that the developed method could be a useful tool for Hg isotope analysis.

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