Supporting Information

The efficiency of Hg cold vapor generation and its influence on Hg isotope analysis by MC-ICP-MS

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Text S1 The effect of HNO₃ concentration

High acid concentrations are shown to cause significant deviations of measured isotope ratios from true values for metal isotope systems that use a pneumatic nebulization sample introduction method, such as Fe isotopes,[1, 2] probably due to changes in instrumental mass discrimination caused by sample acid strength. We observed that the suppression of CVG efficiency increased with the increase of HCl concentration in sample matrix (see Section 3.2.1 in the main text). However, this suppression could be caused by either the high chloride concentration or the high acid strength. To distinguish these two factors, we performed additional experiments that replace HCl with HNO₃, which allows for us to assess the effect of acid strength only. We tested the Hg CVG efficiency and Hg isotope fractionation during CVG at 30% and 50% (v/v) HNO₃ concentrations (corresponding to H^+ concentrations of 4.2 and 7.0 M, respectively) using GLS II. The results showed that sample acidity had no significant influence on Hg isotope analysis using CVG. As shown in Figure S2, the average Hg CVG efficiency at 30% and 50% HNO₃ concentration was 95.9% ± 1.7% (2SD, n = 2) and 95.93% ± 1.8% (2SD, n = 2), respectively. Both $\delta^{202}Hg$ and $\Delta^{199}Hg$ were within the range of uncertainty.

Text S2 Calculation of δ^{202}Hg caused by the NIST 2702 matrix

Since the Hg isotope fractionation caused by the NIST 2702 matrix was most likely caused by incomplete Hg(II) reduction and inhibited Hg(0) volatilization during CVG (see Section 3.2.2), and both processes can be modeled with a Rayleigh fractionation[3], the observed δ^{202}Hg can be calculated using a Rayleigh fractionation equation according to Criss[4] using the experimental Hg isotope fractionation enrichment factors of Hg(II) reduction (ε^{202}Hg $= -1.5$ to -1.8)[5] and Hg(0) volatilization (ε^{202}Hg $= \sim -0.5$)[6]:

$$\frac{\delta^{202}\text{Hg}+1000}{\delta^{202}_{\text{initial}}\text{Hg}+1000} = f^{\alpha^{202}_{\text{g-aq}}\text{Hg}-1} \tag{1}$$

where $\alpha_{\text{g-aq}}^{202}$Hg is the fractionation factor and is calculated from the enrichment factor according to: ε^{202}Hg $= 1000\cdot\ln\alpha^{202}_{\text{g-aq}}$Hg. f is the fraction of remaining reactant, which is equivalent to the suppression of Hg CVG efficiency (calculated as 100% - CVG efficiency). $\delta^{202}_{\text{initial}}$Hg represents the original δ^{202}Hg value of NIST 2702, which is -0.79‰ (Table 1). Therefore, if the suppression of Hg CVG efficiency of GLS I were completely caused by either inhibited Hg(0) volatilization or incomplete Hg(II) reduction, the predicted δ^{202}Hg of GLS I calculated using equation (1) is -1.23‰ and -2.38‰, respectively. The predicted δ^{202}Hg of GLS II calculated using the experimental enrichment factor of Hg(II) reduction is -1.68‰.

Text S3 Calculation of the Hg isotope enrichment factor in the humic acid experiment

In the humic acid experiments, our results showed a generally higher $\delta^{202}Hg$ in the gaseous Hg(0) produced by Hg(II) reduction (i.e, the $\delta^{202}Hg$ in the trapping solution) than the initial $\delta^{202}Hg$ (i.e, the initial $\delta^{202}Hg$ of NIST 3133, which is 0) during CVG, suggesting that heavier isotopes were preferentially reduced. Moreover, $\delta^{202}Hg$ of the Hg that was transmitted (i.e., Hg collected by the trapping solution) decreased linearly toward to the initial $\delta^{202}Hg$ as Hg CVG efficiency increased. These fractionation patterns are consistent with a closed system equilibrium isotope fractionation, which predicts that heavier isotopes tend to enrich in species with a stronger bonding environment and that the isotope ratio of the product shifts linearly toward the starting isotope ratio of the reactant.[7] The equilibrium enrichment factor ($\varepsilon^{202}Hg_{g\text{-}aq}$) is typically determined from the constant difference in $\delta^{202}Hg$ values between the product and reactant ($\varepsilon^{202}Hg_{g\text{-}aq} = \delta^{202}Hg_{product} - \delta^{202}Hg_{reactant}$). In this experiment, the $\delta^{202}Hg_{product}$ refers to the $\delta^{202}Hg$ of Hg(0) reduced from Hg(II) complexed by weak binding sites of humic acid, which is equivalent to the $\delta^{202}Hg$ of the trapping solution, but $\delta^{202}Hg_{reactant}$ could not be measured. However, the equilibrium enrichment factor $\varepsilon^{202}Hg$ can be estimated from intercepts of linear regressions of $\delta^{202}Hg_{product}$ versus the Hg CVG efficiency (i.e., the initial $\delta^{202}Hg_{product}$ at 0% Hg CVG efficiency where $\delta^{202}Hg_{reactant} = 0$). According to Figure S3, the $\varepsilon^{202}Hg_{g\text{-}aq}$ values in the humic acid experiment are 0.31 ± 0.14 and 0.67 ± 0.21 (1SE) for GLS I and GLS II, respectively.
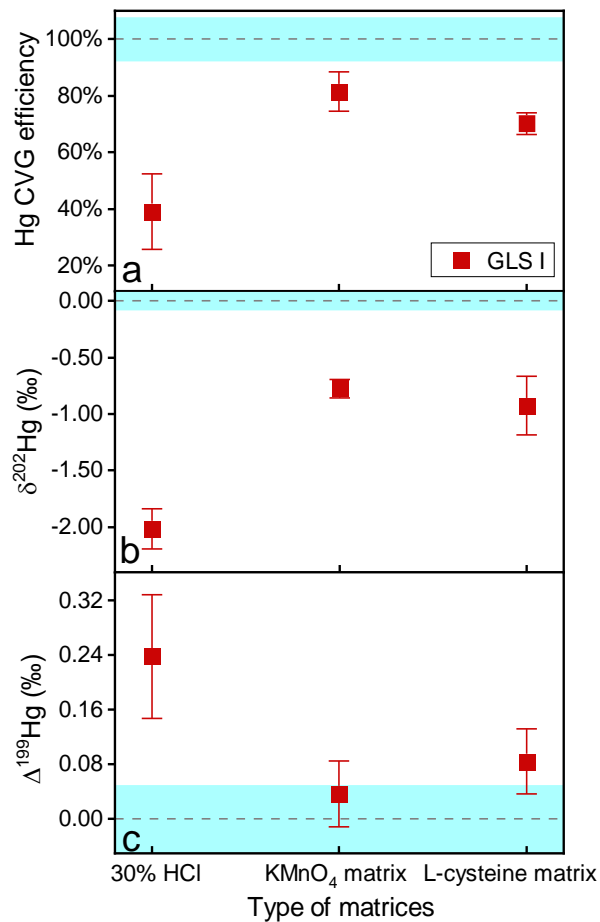
Figure S1. The effects of 30% HCl (3.3M), the KMnO$_4$ matrix and L-cysteine matrix on a) Hg CVG efficiency, b) δ^{202}Hg and c) Δ^{199}Hg at a sample uptake rate of 3.5 mL·min^{-1} for GLS I.
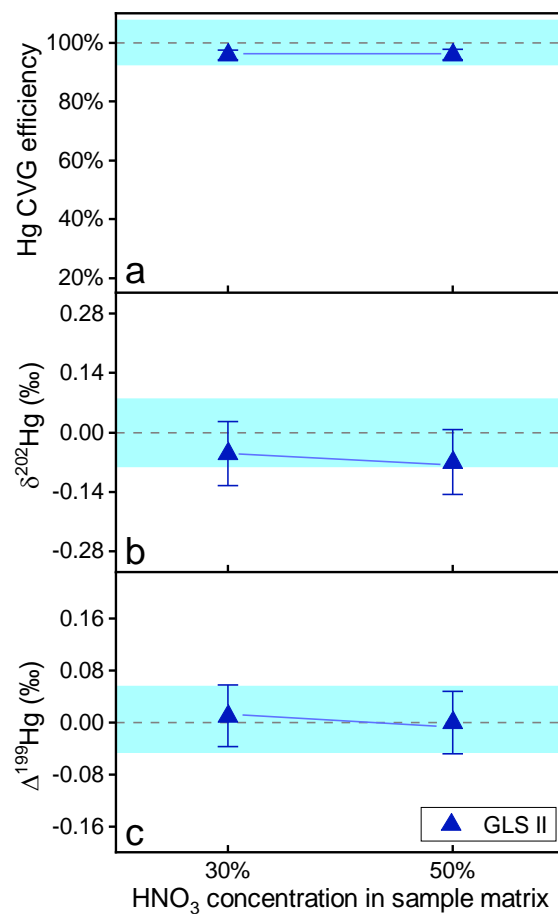
Figure S2. The effect of HNO₃ concentration on a) Hg CVG efficiency, b) δ^{202}Hg and c) Δ^{199}Hg for GLS II.
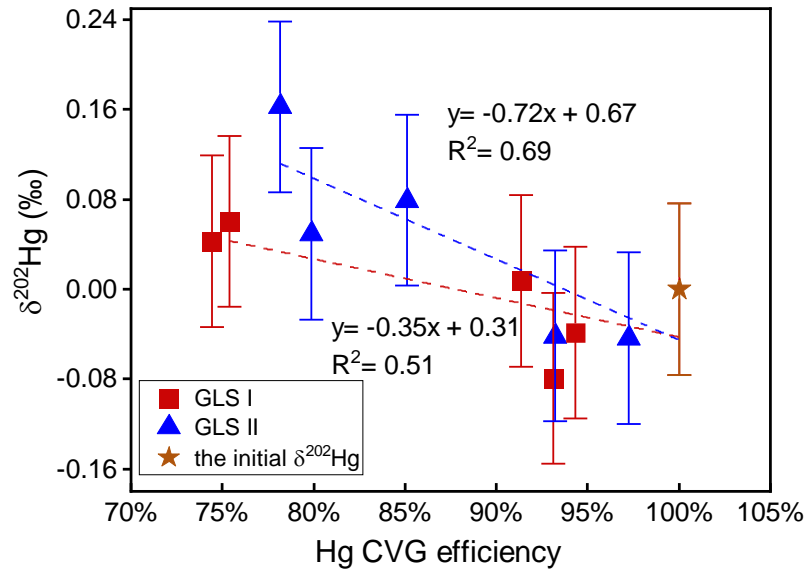
Figure S3. Plots of δ^{202}Hg versus Hg CVG efficiency in the humic acid experiment.

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