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The effect of hydride formation on instrumental mass discrimination in MC-ICP-MS: A case study of Mercury (Hg) and Thallium (Tl) isotopes

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Abstract

Here we report evidence for enhanced hydride formation for Hg isotopes when using high sensitivity X skimmer cones and the Neptune MC-ICP-MS. The effect on the instrumental mass discrimination and the robustness of the Tl external mass-bias correction was investigated. A series of experiments have been conducted to study the effect of variable Hg concentrations on the measured mass bias correction factor, β_{Tl}. The results of our experiments show a linear relation between the Hg concentration and the measured $^{205}Tl/^{203}Tl$ ratio of the internal standard. The resulting mass-bias correction factor β_{Tl} thus appears to be dependent on the analyte concentration, questioning the applicability of Tl as an internal standard for high precision Hg isotope ratio measurements. These observations are consistent with the formation of Hg hydrides (HgH_x where x = 1, 2). Numerical simulations show Hg hydride formation rates of 0.02 to 0.18% to be consistent with experimental observations, when using high-sensitivity X skimmer cones. Here we discuss the implications of Hg hydride formation for Hg isotope ratio measurements and propose a set of precautionary steps that can help to identify and remediate analytical issues related to hydride formation. Whilst the effect of hydride formation on mass-dependent Hg isotope ratios can be controlled, mass independent Hg ratios are shown to be very

sensitive to hydride formation. A comparison between different types of sediment samples and standards also suggests a matrix dependency on hydride formation. We conclude that precise and accurate Hg isotope ratio determination using MC-ICP-MS is possible, however, probably not to low ppm-levels of precision.

Introduction

Multi-collector ICP-MS is the method of choice for high precision isotope ratio measurements. One area of development is improving the overall sensitivity of the technique to reduce the sample quantities needed for accurate and precise isotope ratio measurements. To this end, a number of recent studies have looked at increasing the ion sampling efficiency from the ICP source into the mass spectrometer through the use of modified skimmer and sample cone geometries[1-4], which are often used in combination with enhanced interface pumping configurations.[5-9] Whilst these approaches have afforded an increase in analytical sensitivity, the effect on the instrumental mass bias is not fully understood. Furthermore, the mass bias behavior is element dependent. For example, Newman *et al.*[1,2] reported anomalous mass bias behavior for Nd isotope ratios associated with the increased formation of NdO^+ when using high sensitivity skimmer cones, on both the Thermo Neptune and Nu Plasma MC-ICP-MS instrument platforms. Similar mass bias behavior for Nd has been reported by other groups when using the high sensitivity X skimmer cone and Jet sample cone on the Neptune MC-ICP-MS instrument, with[5] and without[4] enhanced pumping of the interface region. Skimmer and sample cone dependent mass bias behavior has also been reported for other elements. For example, Hu *et al.*[7] reported that the instrumental mass bias for hafnium displayed a large non-linear component, that could not be corrected for using the standard mass fractionation laws, when using the X-skimmer cone and Jet sample cone (on the Thermo Neptune MC-ICP-MS). Lin *et al.*[9] showed that the instrument mass bias was dependent on the specific cone combination used when measuring boron isotope compositions (although the effects reported were not detrimental to the measurement accuracy). In another study, the magnitude of the $\delta^{183}W$ anomalies reported for the tungsten NIST SRM 3163 standard was shown to be dependent on the sample and skimmer cone used.[3]

These studies[1-9] emphasize that the use of enhanced sensitivity ICP-MS interface configurations and the now almost routine reporting of ppm levels of precision for many isotope systems necessitates the careful evaluation of the mass bias behavior of the specific isotope system of interest. The exponential law is the most widely used correction method to determine the true ratio, R_t, from the measured ratio, R_m for isotopes of masses m_1 and m_2, related by a fractionation co-efficient, β ;

$$R_t = R_m \left(\frac{m_2}{m_1}\right)^{\beta} \tag{1}$$

Internal normalization whereby β is determined using a known invariant ratio of two masses (which excludes the isotope of interest) can be used for radiogenic isotope systems[10] (*i.e.* Sr, Nd, Hf), but cannot be applied to stable isotope measurements. For stable isotopes, external normalization against a standard (*e.g.* standard-sample bracketing) of known isotopic composition[10] or a known invariant isotope ratio of another element[11] must be used to correct for the instrumental mass bias. When using the standard-sample-bracketing approach, the sample measurement is bracketed by standard measurements and isotope ratios of the sample are then expressed normalized to the average of the standard measurements. This approach assumes that the mass bias is stable between the sample and standard measurement, and that the sample and standard exhibit the same mass bias behavior, necessitating the use of matrix and concentration matched standards and samples.

External normalization to an admixed element with a similar mass and known isotopic composition can attenuate inaccuracies in the reported isotope ratios due to mass bias drift. This approach requires that the standard and sample are affected in the same way by the instrumental mass bias. However, this is not always the case. For example, differences in the mass bias behavior of thallium and lead are well known and necessitate the use of additional empirical corrections when using Tl as an external standard for measuring Pb isotope ratios.[12] It should be noted that both internal and external normalization to an invariant ratio assumes that the instrumental mass bias is mass dependent (see equation 1). Only standard-sample bracketing may be used to correct for non-linear mass bias and only if the sample and the standard display the same mass independent behavior. One potential contribution to non-linear mass bias in ICP-MS is polyatomic or isobaric ions at the m/z values of interest.

Previous studies[1,2,4,5] have shown that high sensitivity skimmer cones can be associated with increased rates of formation of polyatomic species, that can impart a non-linear component to the instrumental mass bias. In this work, we report the increased formation of Hg hydride species when using the high sensitivity X skimmer cone geometry on the Thermo Neptune instrument, and show how this can lead to inaccuracies in Hg isotope ratio measurements.

The analysis of Hg isotopes using MC-ICP-MS is gaining momentum to further our understanding of sources of mercury contamination and the recycling of inorganic and organic Hg species in the environment.[13,14] The most common analytical approach is the introduction of Hg as gaseous Hg^0 (*i.e.* cold vapor) into the ICP source. Mass bias correction is usually performed using external normalization to a certified thallium standard (NIST SRM 997; $^{205}Tl/^{203}Tl$ ratio of 2.23714), followed by sample-standard bracketing with the NIST SRM 3133 Hg standard.[15] Since Tl does not form a cold vapor like Hg, it is usually introduced as an aerosol and admixed with the Hg cold vapor before the ICP.[16] Assuming neither sample introduction device creates additional mass bias, the Tl standard is used to monitor the instrumental mass bias and to calculate the fractionation co-efficient, β, which is subsequently applied to correct for the instrumental mass bias on the measured Hg isotope ratios.

Thallium appears to be a good candidate as internal standard for Hg isotope ratio measurements; Tl and Hg mass ranges overlap but do not interfere in the form of isobars, so one can assume that $\beta_{Hg} \approx \beta_{Tl}$. However, Hg hydride and dihydride species will form spectral interferences on both the Tl and Hg isotopes. This will invalidate the mass bias correction ($\beta_{Hg} \neq \beta_{Tl}$) and impart an apparent mass-independent isotope signature on the reported Hg isotope ratios. In view of the small (*i.e.* < ~0.5 per mil)[14] natural isotope variations under consideration and reported measurement precision, we show here that even very low rates (<0.2 %) of hydride and/or dihydride formation produce large per mil deviations in the reported Hg isotope ratios.

Experimental Setup

All isotope analyses were performed on a Neptune MC-ICP-MS instrument (Thermo Fisher Scientific, S/N 1006) recently equipped with the *Plus* upgrade, (*i.e.*

Pfeiffer OnTool Booster pump). For most experiments standard Ni sampler cones and either standard H-cones or high sensitivity X-cones were used. In addition, one set of experiments was carried out using a combination of high sensitivity X-skimmer and high efficient Jet sampler cone to fully utilize the Neptune PLUS capabilities of our MC-ICP-MS. Instrumental tuning was checked for and optimized on a daily basis, and gain calibration of the collectors was performed daily and before each set of experiments. Mercury blank contributions were less than 160 pg.

A Cetac HGX-200 cold vapor system was used to generate a Hg^0 vapor by the quantitative reduction of Hg(II) in solution using stannous chloride (3% w/v). The Hg^0 vapor was introduced directly into the ICP. The Tl internal standard was nebulized using a 50 uL min^{-1} self-aspirating micro-concentric PFA nebulizer and either an ApexQ system or an SSI spray-chamber (both from Elemental Scientific Inc.). The resultant Tl aerosol was then admixed to the flow from the cold vapor system using 3/8" O.D. Y-shaped connector. The Hg beam intensities were independent of the introduction system used for the Tl. The ApexQ gave approximately an order of magnitude increase in the Tl beam intensities. However, the combination of the HGX-200 cold vapor system and SSI spray-chamber gave the most stable ion beam intensities and instrumental mass bias for both Hg and Tl isotope beams.

The NIST 1944 sediment standard and lake sediment samples (0.2 – 0.6 g) were digested using 10 mL aqua regia in a 40 mL open glass vessel by heating on a hot plate at 120°C for 4 hours. After digestion, all samples were centrifuged and the supernatant was extracted and made up to 40 mL with 0.02 M BrCl solution. Digested samples were stored refrigerated at 4°C prior to analysis.

As recommended by Blum and Bergquist,[14] the Hg isotope ratios are reported in δ notation relative to the NIST SRM 3133 Hg bracketing standard:

$$\delta^{xxx}\mathrm{Hg}(‰) = ([(^{xxx}\mathrm{Hg}/^{198}\mathrm{Hg})_{\mathrm{unknown}} / (^{xxx}\mathrm{Hg}/^{198}\mathrm{Hg})_{\mathrm{SRM3133}}] - 1 \text{ x } 1000$$

The magnitude of any mass independent fractionation (Δ^{xxx}Hg) is derived from the measured δ-value and the kinetic mass dependent fractionation law.[15] The NIST SRM 1944 New Jersey Water Way Sediment standard and UM-Almadèn (kindly provided by J. Blum, University of Michigan) cinnabar standard were measured to check the data accuracy (Table 1) and are in good agreement with the values reported by other groups.[14, 17-19] All Hg solutions were prepared in 1M HCl + 0.02M BrCl using only high purity reagents. Stannous Chloride solutions (3% w/v) were prepared in 1M HCl and purged with Ar gas for 30 minutes before the experiments. For the Tl standard we used a 10-200 ppb standard ICP-MS tuning solution diluted in 0.3M HNO$_3$ (~2% v/v) from 1000 ppm stock solutions, with an assumed ^{205}Tl/^{203}Tl ratio of 2.38698. The exact ^{205}Tl/^{203}Tl ratio used to determine β_{Tl} is not critical as the Hg isotope values are reported in delta notation relative to the NIST SRM 3133 Hg standard.

	δ^{199}Hg	δ^{200}Hg	δ^{201}Hg	δ^{202}Hg	Δ^{199}Hg	Δ^{201}Hg	N
[a]UM-Almaden	**−0.14±0.05**	**−0.26±0.08**	**−0.47±0.03**	**−0.54±0.08**	**−0.01±0.04**	**−0.07±0.08**	**12**
[b]UM-Almaden	−0.14±0.06	−0.27±0.04	−0.44±0.07	−0.54±0.08	−0.01±0.02	−0.04±0.04	25
[c]UM-Almaden	−0.14±0.11	−0.23±0.14	−0.40±0.13	−0.48±0.16	−0.01±0.08	−0.03±0.07	54
[a]NIST1944*	**−0.11±0.08**	**−0.21±0.11**	**−0.36±0.14**	**−0.44±0.15**	**0.00±0.06**	**−0.03±0.11**	**25**
[c]NIST1944	−0.10±0.02	−0.23±0.23	−0.38±0.18	−0.48±0.29	0.02±0.05	−0.01±0.04	3
[d]NIST1944				−0.42±0.07		−0.02±0.01	10
[e]NIST1944				−0.45±0.06		−0.03±0.02	5

Table 1: Hg isotope data for selected reference materials UM-Almanden and NIST SRM 1944 New York/New Jersey Waterway Sediment Standard. Data are given as deviation in ‰ from the ^{x}Hg/^{198}Hg ratio of NIST SRM 3133 Mercury Standard. Uncertainties are given as 2x the standard deviation. Tl/Hg ~5

* data obtained from 12 full procedural repeats using NIST SRM 1944

[a] This work, [b] ref 14 [c] ref 17 [d] ref 18 [e] ref 19

Results

Table 2 gives the δHg and ΔHg values determined for three different concentrations (2, 5 and 10 ppb) of the UM-Almandèn cinnabar standard measured relative to a 5 ppb NIST SRM 3133 mercury standard solution. The ratio of the Tl to Hg total ion beam intensities in the NIST standard was constant (~ 5, see Table 2). The Tl to Hg ratio for the UM-Almandèn cinnabar standard varied from 0.9 to 20.2. It is clear that Tl to Hg ratio can have a large effect on the measured Hg isotope composition. The δHg and ΔHg values determined for concentration matched standards are in agreement with published literature values.[14,17]

Hg conc.	Tl/Hg$_{sam}$	Tl/Hg$_{STD}$	δ^{199}Hg	δ ^{200}Hg	δ ^{201}Hg	δ ^{202}Hg	Δ^{199}Hg	Δ^{201}Hg
2 ppb	20.2	5.1	-0.39±0.06	-0.55±0.13	-0.74±0.05	-0.86±0.14	-0.12±0.06	-0.09±0.07
5 ppb	5.6	5.3	-0.14±0.05	-0.26±0.08	-0.47±0.03	-0.54±0.08	0.02±0.04	-0.06±0.05
10 ppb	0.9	5.0	0.01±0.04	0.01±0.04	-0.03±0.03	-0.05±0.03	0.03±0.03	0.00±0.02

Table 2: Hg isotope data for UM-Almandèn. Data are given as deviation in permil from the ^{xxx}Hg/^{198}Hg ratio of a 5 ppb NIST SRM 3133 Mercury Standard. Uncertainties are given as 2x the standard deviation.

To investigate the origin of the observed dependence of the Hg isotope compositions on Tl ion beam intensity a series of NIST SRM 3133 Hg standard solutions with increasing concentrations (1, 5, 10 and 25 ppb) were measured. The β_{Tl} was determined for each Hg standard solution concentration, using the exponential mass bias law (equation 1). Figure 1 shows a plot of the relative change in β_{Tl} (referred to here as $\Delta\beta_{Tl}$) as a function of the Hg concentration (normalized to the β_{Tl} value for the 1 ppb Hg standard), for different concentrations of the Tl internal standard, using the SSI and ApexQ sample introduction systems. The figure shows a strong linear correlation between the calculated mass-bias correction factor β_{Tl} and the Hg standard concentration. The observed line gradients are inversely proportional to the total Tl ion beam intensity *i.e.* deviations in the measured Hg isotope ratios would be expected to be larger for lower concentrations of the Tl standard.

By comparison to the Apex Q system, the SSI system is associated with an increase in solvent loading of the plasma. A plot of the gradient of the lines given in Figure 1 against the reciprocal of the total Tl beam intensity gives a linear correlation (Figure 2), suggesting that the observed dependence of the $\Delta\beta_{Tl}$ value on the Hg concentration is a function of Tl/Hg beam intensity ratio rather than the sample introduction system used for the Tl.

The $\Delta\beta_{Tl}$ value as a function of the Hg concentration is also dependent on the skimmer (and sampler) cone used. For comparable total Tl ion beam intensities (21 V for the X skimmer cone and 17 V for the H skimmer cone for 30 ppb and 200 ppb total Tl respectively), the gradient obtained for a plot of $\Delta\beta_{Tl}$ versus Hg concentration when using the X skimmer cone was approximately twice that observed when using the H skimmer cone (Figure 1). It should be noted that the X cone gave an approximate seven-fold increase in the sensitivity compared to the H cone geometry for Tl (using the ApexQ), however, the increase in sensitivity for Hg is only 10-20%. The combination of high-sensitivity X-skimmer and Jet sampler cones produced the most significant effect, as shown by the steepest slope in figure 1.

The β_{Tl} value also appears to be dependent on the sample matrix. Figure 3 shows the $\Delta\beta_{Tl}$ value as a function of Hg total beam intensity (normalized with respect to the 5 ppb Hg bracketing standard solution) for the NIST 3133 and NIST 1944 standards and a series of lake sediment samples. All data presented in Figure 3 were collected in a single measurement session, using the same instrument setup and $SnCl_2$, Tl and Hg standard solutions. The X skimmer cone was used and a 10 ppb Tl internal standard was introduced using the SSI system. The sediment samples were bracketed by a 5 ppb NIST SRM 3133 Hg standard. The samples and standards were not concentration matched. As seen for the NIST 3133 standard (Figure 1), the $\Delta\beta_{Tl}$ was found to vary with the concentration of Hg in the sediment samples. However, compared to the NIST 3133 standard, the sediment samples plot on a secondary, steeper slope, which would imply that the sample matrix also influences the β_{Tl} value. However, the NIST 1944 sediment standard (used as a secondary standard to check data accuracy) appears to behave in a similar manner to the NIST 3133 standard (see Figure 3 inset).

Discussion

From the standard data given in Table 1 and Figure 3, it is clear that comparable Hg isotope ratios can be measured when using Tl as an internal standard for mass bias correction, combined with standard-sample bracketing, provided that the standard and sample are concentration matched. However, from the data presented in Figure 1, it is also clear that β_{Tl} does depend on the Tl/Hg ratio when the formation of Hg hydrides is occurring. A difference in the Hg concentration of only a few percent between a sample and the standard could result in under- or over-correction of instrumental mass fractionation and confer an artificial bias in the reported Hg isotope ratios of several per mil.

The experiments show that an increase in the Hg beam intensity is associated with a decrease in the measured $^{205}Tl/^{203}Tl$. The relative change in the $^{205}Tl/^{203}Tl$ was found to be greater when using the X skimmer cone (compared to the H cone) for comparable Tl and Hg ion beam intensities. The observed dependence of the $^{205}Tl/^{203}Tl$ ratio on the Hg concentration is consistent with contributions to the measured beam at m/z 205 and 203 from Hg species *e.g.* the formation $^{202}HgH^+$, $^{201}HgH_2^+$ and $^{204}HgH^+$ ions. Monitoring m/z 205 and 203 in the absence of Tl (*i.e.* aspirating a blank 2% HNO_3 solution) showed that the change in β_{Tl} is associated with an increase in the apparent ^{203}Tl beam intensity; an increase of 2.4 mV over the background signal was observed for a Hg concentration of 25 ppb (total Hg signal of ~ 24 V), which corresponds to average Hg-hydride formation rates of 0.1% (for HgH_2) or 0.05% (for HgH). There was no discernible increase on ^{205}Tl beam intensity over background, which suggests the interfering-Hg species affects only the ^{203}Tl signal. This would support the formation of the HgH_2^+ species and could explain the data observed in our experiments. Contributions from HgH^+ species cannot be ruled out, but our observations are consistent with HgH_2^+ being the dominant Hg hydride species formed in this study. Similar tests did not provide evidence for the formation of Tl hydrides.

The formation of Hg hydride species could result in either a relative decrease or increase in the measured abundance of a specific Hg isotope, which would be the sum of losses through the formation of hydride species and any contributions from hydride species of lower mass Hg isotopes. This would confer a mass-independent isotope effect associated with the measurement process on the natural isotope abundances. The Hg $^1S_0$ ground state is relatively unreactive in the gas phase. However, the ^3P and ^1P excited electronic states are known to form the HgH_2 and HgH species in gas phase reactions with atomic H and H_2.[20,21] Excited electronic states of Hg will be readily formed in the ICP (indeed the excitation and subsequent emission of atoms and atomic ions is exploited in ICP-OES), and given that the quenching of the $^3P_0$ state is slow in argon,[22] the Hg $^3P_0$ state in particular would have a sufficient lifetime to participate in reactions and form hydride species. The observed dependence on the geometry of the skimmer cone would support the formation of Hg hydride species during the sampling process in the supersonic expansion. It is now generally accepted that the idealized model of the skimmer inserted into the zone of silence in the supersonic expansion through which the plasma flows unaltered is not realized in practice.[23] Previous studies have suggested that the skimmer may act as a source of a secondary expansion and result in various collision induced processes including the formation of new molecular species (*i.e.* oxides),[1,2] collision-induced dissociation of polyatomic ions (formed in the ICP) and ionization of neutral species.[24]

It is generally accepted that Hg cold vapor generation is free from matrix effects; only Hg vapor is produced using the $SnCl_2$ reductant and as such no pretreatment of the digested samples is required. However, a matrix effect is clearly discernible in the β_{Tl} value. Excited states of Hg are known to be quenched by hydrocarbons via a hydrogen abstraction reaction to form the HgH species.[25] The secondary, steeper slope observed in Figure 3 for the lake sediment samples, indicating a larger relative change in the β_{Tl} values, would suggest an increased rate of formation of the Hg hydride species by comparison to the standards. Typically, for complete conversion of all organic material to CO_2 requires H_2SO_4 or persulfate digestion. Therefore, we propose that for the lake sediment samples measured in this work, trace levels of volatile hydrocarbons are introduced into the plasma concomitantly with the Hg cold vapor and subsequently contribute to hydride formation in the plasma.

Modeling Hg hydride formation and related mass-bias effects

The effect of mercury dihydride formation on the $^{205}Tl/^{203}Tl$ ratio was modeled and compared to experimental data presented here. We first consider the formation of the dihydride species based on the observed increase in the apparent ^{203}Tl signal with increasing Hg concentration (consistent with the formation of $^{202}HgH_2^+$ species) and the expected greater stability of the HgH_2 species compared to HgH.[20] The effect of hydride formation on the observed $^{xxx}Hg^+$ ion beam intensity can be described as follows:

$$ {}^{i}\mathrm{Hg}_{\mathrm{H2}} = {}^{i}\mathrm{Hg}_{0} - \left({}^{i}\mathrm{Hg}_{0} \times f\right) + {}^{i-2}\mathrm{Hg}_{0} \times f = {}^{i-2}\mathrm{Hg}_{0} \times f - {}^{i}\mathrm{Hg}_{0} \times \left(1 - f\right) \qquad (2) $$

Here *i* represents the Hg isotope in question and *i-2* the isotope two masses below isotope *i*, $^{i}Hg_{H2}$ is the abundance of ^{i}Hg taking into account formation of dihydrides (*f*), $^{i}Hg_0$ is the abundances of respective isotopes prior to hydride formation.

Mercury isotopes ^{196}Hg and ^{199}Hg have no Hg isotopes two masses below and will therefore not experience an increase due to addition of dihydride formation, but only a loss:

$$^{i}\mathrm{Hg}_{\mathrm{H2}} = {}^{i}\mathrm{Hg}_{0} - \left({}^{i}\mathrm{Hg}_{0} \times f\right) = {}^{i}\mathrm{Hg}_{0} \times \left(1 - f\right) \qquad (3)$$

Therefore, the abundance of the ^{203}Tl isotope will change according to equation (4):

$$^{203}\mathrm{Tl}_{\mathrm{H2}} = {}^{203}\mathrm{Tl}_{0} + {}^{201}\mathrm{Hg}_{0} \times f \qquad (4)$$

and ^{205}Tl will remain unaffected.

Considering the extended isotope space of Hg and Tl, a system of nine equations emerges, which can be expressed in matrix form:

$$\begin{bmatrix} (1-f) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ f & (1-f) & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & (1-f) & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & f & 0 & (1-f) & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & f & 0 & (1-f) & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & f & 0 & (1-f) & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & f & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & f & 0 & (1-f) & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} ^{196}\mathrm{Hg} \\ ^{198}\mathrm{Hg} \\ ^{199}\mathrm{Hg} \\ ^{200}\mathrm{Hg} \\ ^{201}\mathrm{Hg} \\ ^{202}\mathrm{Hg} \\ ^{203}\mathrm{Tl} \\ ^{204}\mathrm{Hg} \\ ^{205}\mathrm{Tl} \end{bmatrix}_{0} = \begin{bmatrix} ^{196}\mathrm{Hg} \\ ^{198}\mathrm{Hg} \\ ^{199}\mathrm{Hg} \\ ^{200}\mathrm{Hg} \\ ^{201}\mathrm{Hg} \\ ^{202}\mathrm{Hg} \\ ^{203}\mathrm{Tl} \\ ^{204}\mathrm{Hg} \\ ^{205}\mathrm{Tl} \end{bmatrix}_{\mathrm{H2}}$$

The formation rate of hydrides is given by coefficient f. Multiplying the isotope space vector $[\mathrm{Hg,Tl}]_0$ by the formation matrix (here shown for di-hydride formation) yields the hydride affected isotope space $[\mathrm{Hg,Tl}]_{\mathrm{H2}}$ for a given value of f. Isotope ratios and beta factors can then easily be computed using the isotope abundances. A similar matrix can be constructed for the mono-hydride species.

Implications of hydride formation for Hg isotope ratio measurements

Formation of Hg-hydride species inevitably produces a concomitant mass-independent shift in the mercury isotope abundances and also interferes with Tl masses. Firstly, considering Hg ratios only and ignoring instrumental mass-bias; the measured isotope ratios can be significantly offset from the respective “true” ratios (Figure 4). Here we focus for simplicity on only the mass-dependent δ^{202}Hg values, as well as mass-independent $\Delta^{199,201}$Hg ratios, and the offset form the true value caused by shifting the relative isotope abundances due to hydride formation (for mono- as well as di-hydride formation). Even very low hydride formation rates (< 0.2%) can create a significant offset in the measured mass-dependent δ^{202}Hg value, as well as in mass-independent Hg isotope ratios. However, it must be stressed that these effects are suppressed, when samples are carefully bracketed and the formation rate is constant for samples as well as the bracketing standards. This would represent the case where the isotope abundances of the bracketing standard and the sample are shifted in similar proportions and the net effect when calculating δ-values (and resulting Δ-values) is negligible. That the hydride formation rate is, on our instrument, most likely constant during a short bracketing interval (standard-sample-standard) is probably a reasonable assumption, given the high degree of linearity and thus repeatability of our experiments (see Figures 1 & 2). On the contrary, if the hydride formation rate varies between sample and bracketing standards, the effects on δHg and ΔHg values can be significant.

For the next case we consider the Tl corrected Hg isotope ratios. Because Tl and Hg mass-ranges overlap, Hg-hydride species can interfere with both Tl isotopes (mono-hydride formation) or only the ^{203}Tl isotope (di-hydride formation). In either case, the analyte is directly changing the isotope composition of the internal standard and hence the value β_{Tl}. Figure 5 shows a sensitivity analysis for mercury dihydride formation and the resulting offset in β_{Tl} values as a function of hydride formation rate f, as well as the Tl/Hg ratio. The experimental data (blue dots in Figure 5) can be simulated with dihydride formation rates between 0.02% and 0.18%, which is also consistent with the empirical Hg-hydride formation rates obtained from the increase of the ^{203}Tl background. Even these very low hydride formation rates have a significant impact on the isotope ratio of the internal standard, which will propagate through to produce comparatively large offsets in Tl-corrected δ^{xxx}Hg values (Figure

6). Two observations emerge; (i) Tl-corrected ratios can show even larger offsets for a given rate of hydride formation, and (ii) the Tl/Hg ratio is crucial in determining the sensitivity of the offset and how well Hg concentrations should be matched between samples and standards. In general, Tl/Hg ratios should be relatively high to minimize the effect of Hg-hydride addition to the Tl isotope masses and also to allow for a wider tolerance in terms of Hg concentration matching (this is when the curves in Figure 6 are horizontal). The mass-independent Hg values are insensitive to the chosen Tl/Hg ratio, and are identical to the offsets shown in Figure 5. In this more complex case, the Tl corrected Hg isotope ratios are sensitive to the hydride formation rate as well as the Tl/Hg ratio, and precise and accurate Hg isotope ratio measurements require careful evaluation of hydride formation rates as well as optimized running conditions as far as Tl and Hg concentrations are concerned. Measuring the magnitude of natural isotope fractionation is the main reason for employing high precision MC-ICP-MS techniques. However, natural isotope fractionation will change the relative isotope abundances of stable Hg isotopes, and thus the relative contribution of Hg-hydride species to neighboring isotope masses. In the above examples, we have evaluated the effect of different Hg concentrations as well as Tl concentrations, assuming the isotope composition of the material is not fractionated with respect to the bracketing standard. Considering now the case of a Tl/Hg intensity ratio of 0.5, hydride formation rate $f = 0.2$, and a modest natural isotope fractionation of $\alpha = 0.02$. The additional offset in β_{Tl} created by a different natural isotope composition of the sample means that Tl-corrected δ^{202}Hg ratio is ~ +0.4‰ higher than the non Tl-corrected δ^{202}Hg ratio (Figure 7). This is due to the different isotope abundance of the fractionated sample, especially its higher ^{201}Hg abundance, which produces larger $^{201}HgH_2$ interference on ^{203}Tl, and therefore a slightly different correction factor β_{Tl} compared to the bracketing standard. The corresponding change in β_{Tl} between the bracketing standard and the fractionated sample is relatively minor (+0.02), and could easily be dismissed as instrumental noise. This additional offset is reduced by an order of magnitude (to ~0.01‰), when the Tl/Hg ratio is increased to 20. Given that Hg isotope data are now typically reported to ppm-level precision and accuracy, this apparent minor change in the Tl fractionation correction factor can lead to a significant discrepancy between the actual Hg isotope ratio and the reported ratio.

For constant hydride formation rates, effective measures to reduce the artificial isotope effect on mass-dependent isotope ratios include (i) adjusting the Tl/Hg ratio and (ii) concentration matching Hg in samples and bracketing standards. Mass-independent isotope ratios can be very sensitive to variable hydride formation rates (Figure 8). The offsets in figure 8 are independent of Tl and Hg concentration, but are solely a function of differences in the hydride formation rates between sample and bracketing standard. For example, if the formation rate of di-hydrides in the sample was +0.04% higher than the standard, the mass-independent Δ^{199}Hg and Δ^{201}Hg differ by -0.08‰ and +0.28‰, respectively, and this cannot be corrected for by concentration matching Hg or increasing Tl/Hg ratios.

It should be noted that a poor abundance sensitivity of the mass analyzer could also produce a similar change of the ^{203}Tl/^{205}Tl ratio as a result of tailing from ^{204}Hg onto ^{203}Tl. Writing a matrix and taking into account the contribution from ^{204}Hg onto ^{203}Tl as abundance sensitivity degrades, shows that the experimental data from Figure 1 can only be explained by ion scattering when the abundance sensitivity of the mass analyzer is between 1000 and 5000 ppm. This is at least three orders of magnitude greater than abundance sensitivity of our instrument (<10 ppm) and can therefore be discounted.

Conclusions and Implications

We have observed subtle but systematic offsets in Tl-corrected Hg isotope ratios and attribute these to isobaric interferences from HgH_x (where x = 1,2) species on the Tl isotope masses. The determination of Hg isotope ratios using Tl as an internal standard for mass bias correction can be compromised by relatively small differences in the Hg concentration (*i.e.* a few percent), as well as natural isotope fractionation between a sample and the standard, which can lead to an under- or over-correction of instrumental mass fractionation and confer a bias in the reported mass-dependent Hg isotope ratios of several tenths of permil. Assuming that the rate of Hg hydride formation is the same for standards and samples, then careful concentration matching and choosing suitable Tl/Hg ratios will largely mitigate these effects, even if hydride formation rates are not identical for standards and samples. However, differences in hydride formation rates for standards and samples can create significant artificial mass-independent isotope effects, which are impossible to correct for. Although speculative, such artificial mass-independent isotope effects could be reproducible and sample dependent, based on our observation that hydride formation could be sample and matrix specific (in the absence of any pre-treatment).

In addition to adjusting Tl and Hg concentrations, the choice of skimmer and sampler cones can also help to mitigate the effects of hydride formation. The standard H-cones on the Neptune *PLUS* MC-ICP-MS were shown to be associated with significantly lower rates of Hg hydride formation when used in tandem with standard Ni sampler cones. Switching to high sensitivity X-skimmer cones does not improve Hg beam intensities much (10-20%), but greatly increases the formation rates of Hg hydrides and thus non-linear mass bias effects. Utilizing the full *PLUS* capabilities of our Neptune MC-ICP-MS by using high sensitivity S-skimmer and Jet sampler cones in tandem produces even higher hydride formation rates. Hydride formation rates are on average 0.12% when using the X-skimmer and standard sampler, but double in magnitude (~0.45%) when using X-skimmer and Jet sampler cones, whilst Hg beam intensities increase by merely 10%. Whilst the overall Tl mass-bias is somewhat lower with the Jet cones (~ -0.9% as opposed to -1.2/-1.3 for X-skimmer/H-skimmer and standard sampler cone), non-linear mass bias effects due to hydride formation are greatly enhanced. At least for Hg isotope analyses, the combination of high sensitivity cones (X-skimmer and Jet sampler) and OnTool Booster pump does not confer any analytical merits. Based on our findings, we recommend forgoing the use of high-sensitivity cones and to use standard H skimmer and Ni sampler cones for Hg isotope measurements.

Even though we found evidence of Hg-hydride formation on our Neptune *PLUS* instrument, we do not propose that this is a general phenomenon on MC-ICP-MS instruments. However, based on our findings we recommend a few precautionary steps to be taken to identify and if necessary to reduce the effects of hydride formation. A simple calibration using increasing Hg concentrations for a given Tl concentration can reveal the existence and magnitude of such effects on any instrument. If β_{Tl} changes systematically with Hg concentration, Hg hydrides most likely form in or behind the ICP interface region. A change to low-sensitivity cones may already be sufficient to suppress these effects. In addition, Hg concentrations and Tl/Hg ratios can be carefully matched and adjusted to further mitigate artificial mass-bias effects. However, the change in natural isotope abundance in fractionated samples and an unstable hydride formation rate may still be sufficient to produce offsets in the Tl and hence Hg isotope ratios. Based on the good reproducibility of our experiments, we conclude that accurate Hg isotope determination via MC-ICP-MS is possible, however, not to single digit ppm-level precision.

Although we only evaluated the case of Hg and Tl isotopes, hydride formation may have implications for other isotope systems in cases where elements are prone to hydride formation and analyte and spike isotope masses overlap, *e.g.* Pb isotopes and Tl as an external standard. A quick calibration, similar to the experiments performed here, can reveal if hydride species might pose an issue.

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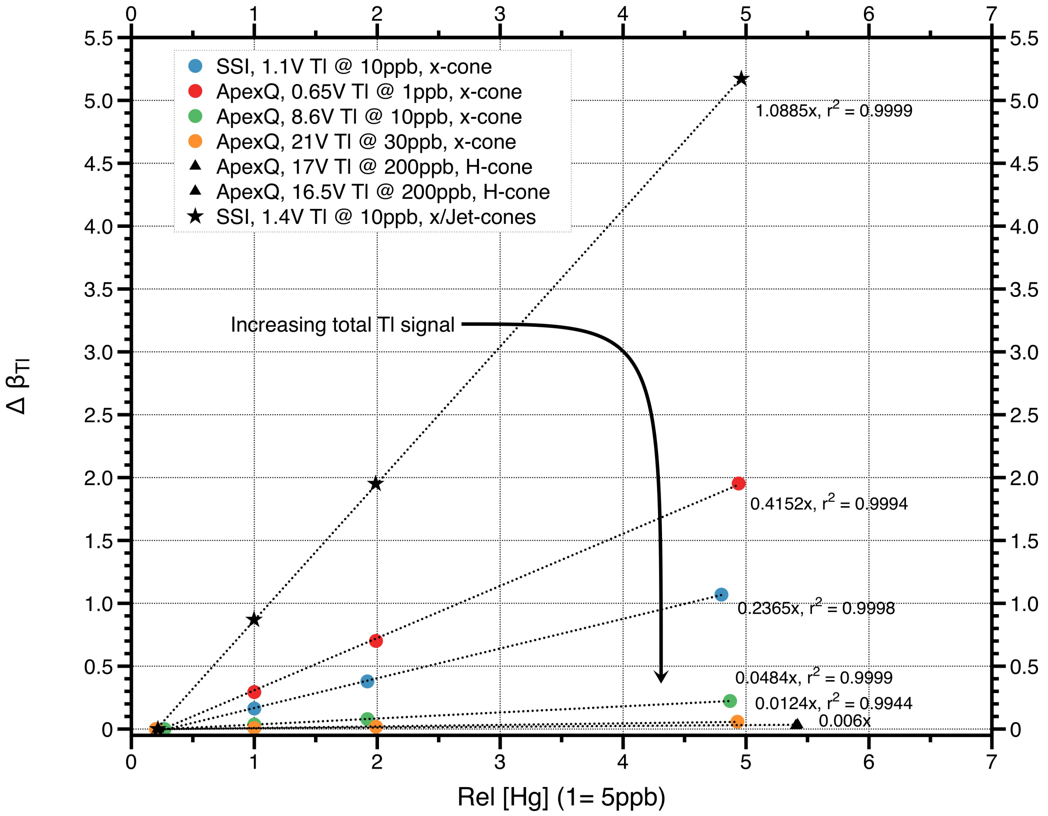

Figure 1: The offset in measured β_{Tl} as a function of increasing Hg concentration. Each plot represents a series of NIST SRM 3133 analyses at increasing Hg concentrations for a given Tl concentration. In each experiment, β_{Tl} increases with increasing Hg concentration. Gradients of plots are inversely correlated with overall Tl concentration. Effect of changing Tl mass-bias is smallest for H-cones. The most sensitive correlation has been found when fully utilizing the capabilities of the Neptune *PLUS* Jet interface.

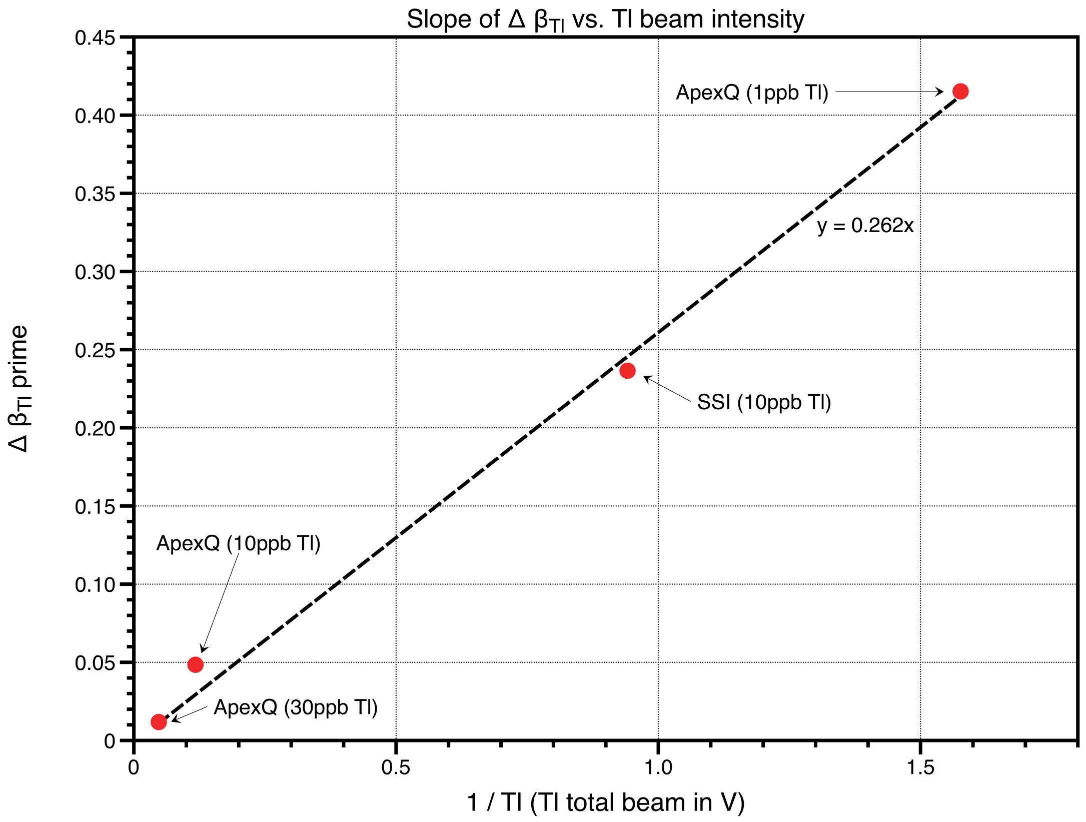

Figure 2: The slopes of the experimental data from figure 1 (x-cones) as a function of Tl beam intensity. The choice of sampling introduction system, e.g. wet vs. dry plasma, has no effect on the observed change in beta-Tl.

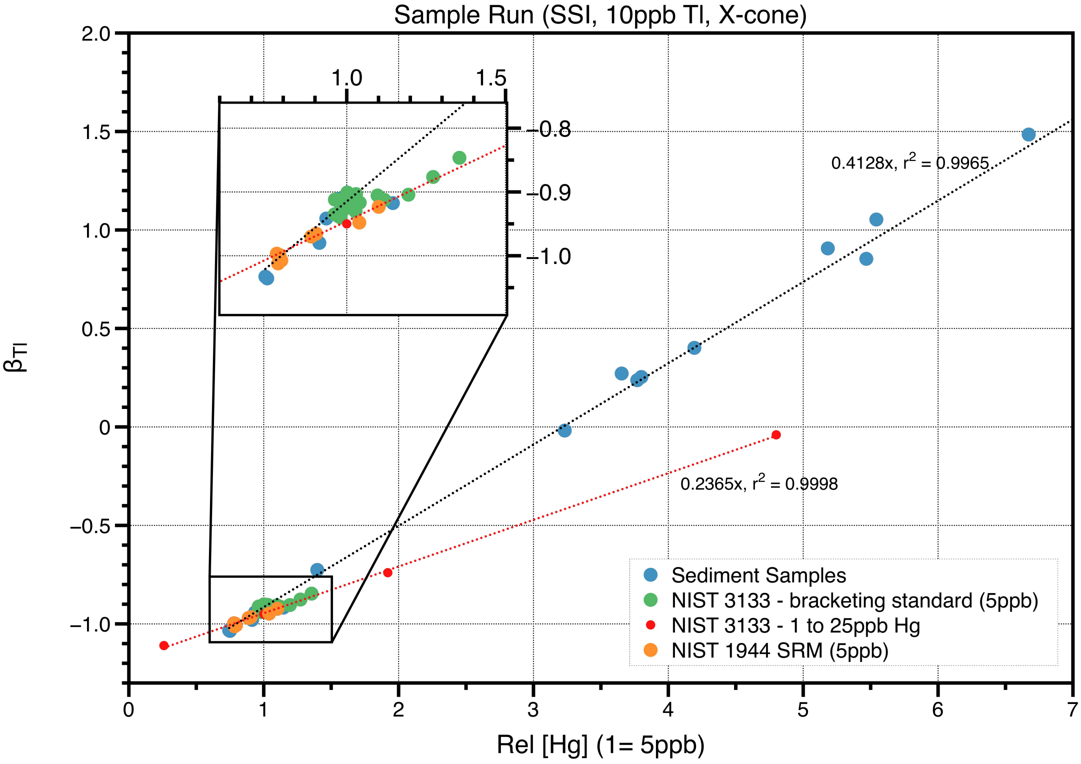

Figure 3: The offset in beta-Tl for a series of real sediment samples (blue dots), as well as NIST SRM 3133 Hg isotope standard (red and green dots) and NIST SRM 1944 New Jersey Water Way Sediment reference material (orange dots). All runs were carried out using the exact same sampling setup and set of reagent solutions. The Hg beam intensity of the NIST materials is changing slightly throughout the run, the change in Tl mass bias is in accord with experimentally observed behavior (red dotted line, see inset).

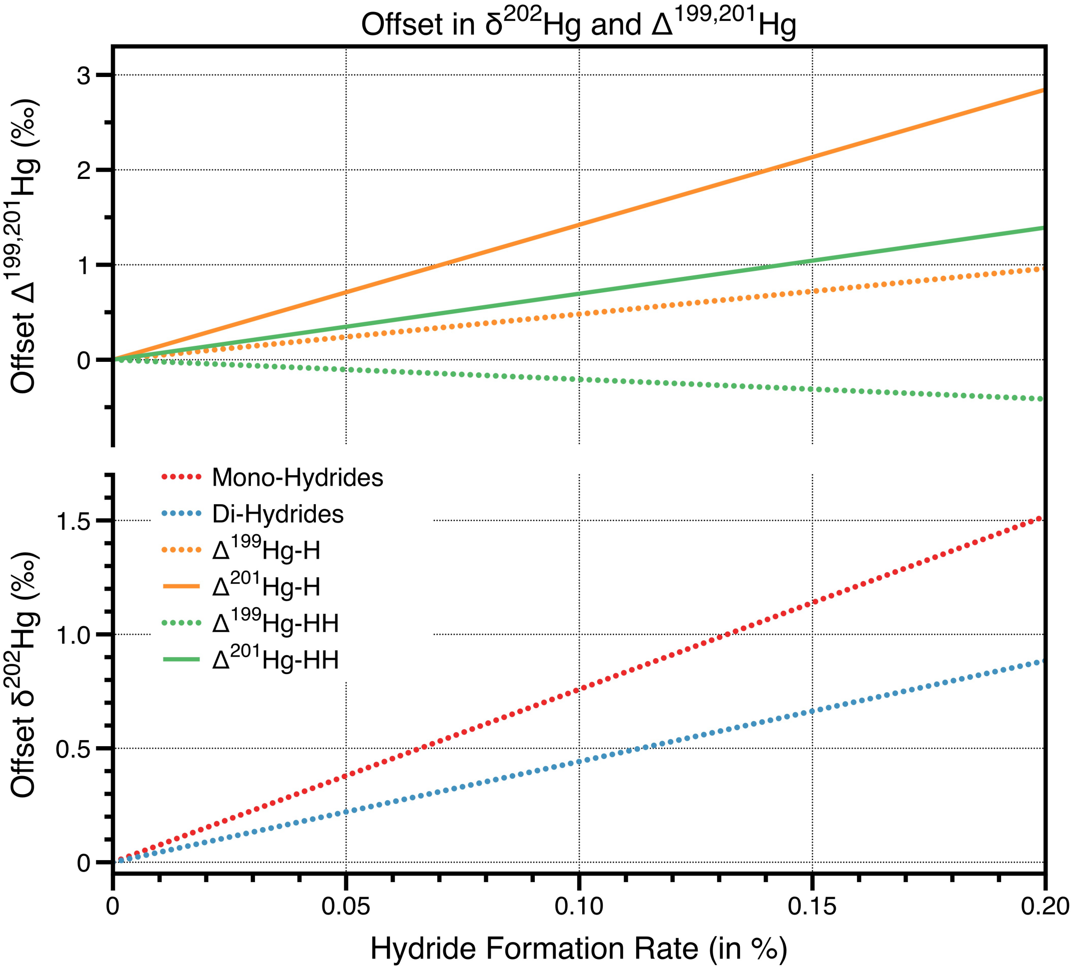

Figure 4: The formation of Hg hydrides produces a shift in the abundances of Hg isotopes and as a result the measured isotope ratios (here given as mass dependent δ^{202}Hg in the lower panel and mass independent $\Delta^{199,201}$Hg ratios in the upper panel) are offset when compared to the “true” isotope ratio. Respective offsets are shown for Hg mono- and di-hydrides, formation rates 0 to 0.2%.

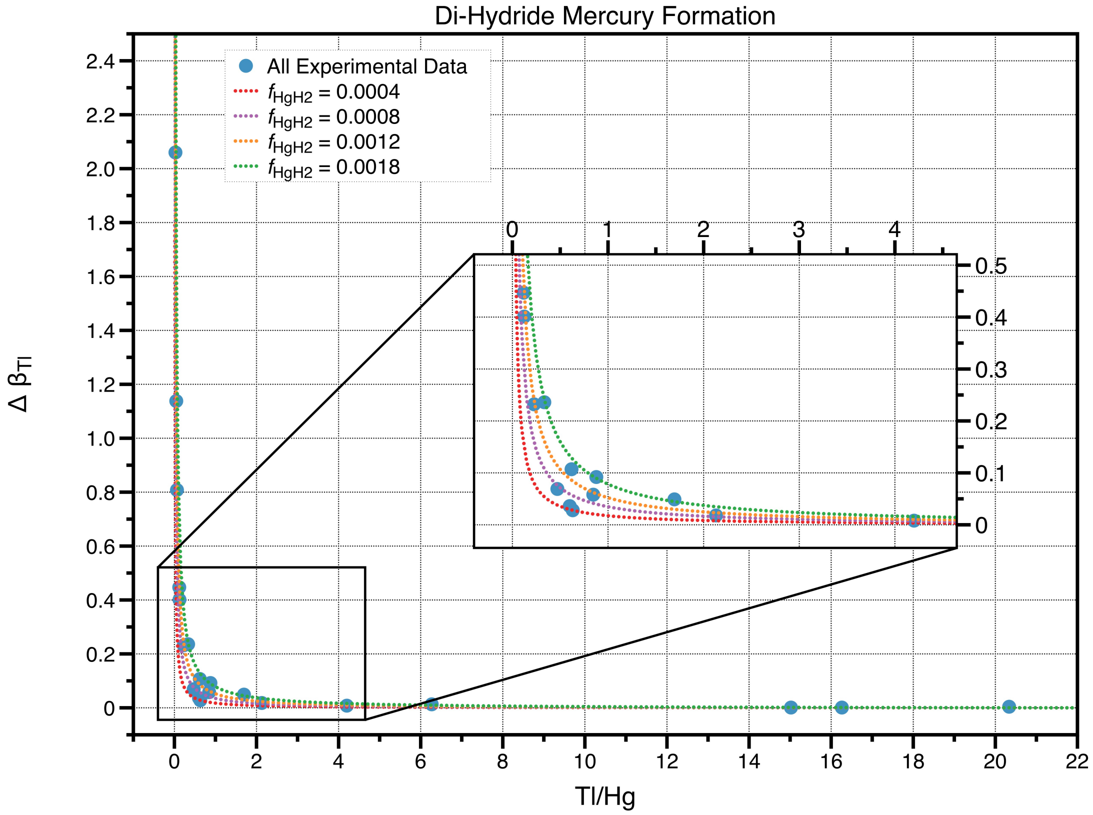

Figure 5: The absolute change in beta-Tl as a function of HgH_2 formation rate and the used Tl/Hg ratio. The effect of HgH_2 formation on the measured $^{203}Tl/^{205}Tl$ ratio is lower the higher the Tl/Hg intensity ratio. Experimental data from figures 1 and 2 (blue dots) are matched to model results when formation rates HgH_2 are between 0.04 and 0.18%.

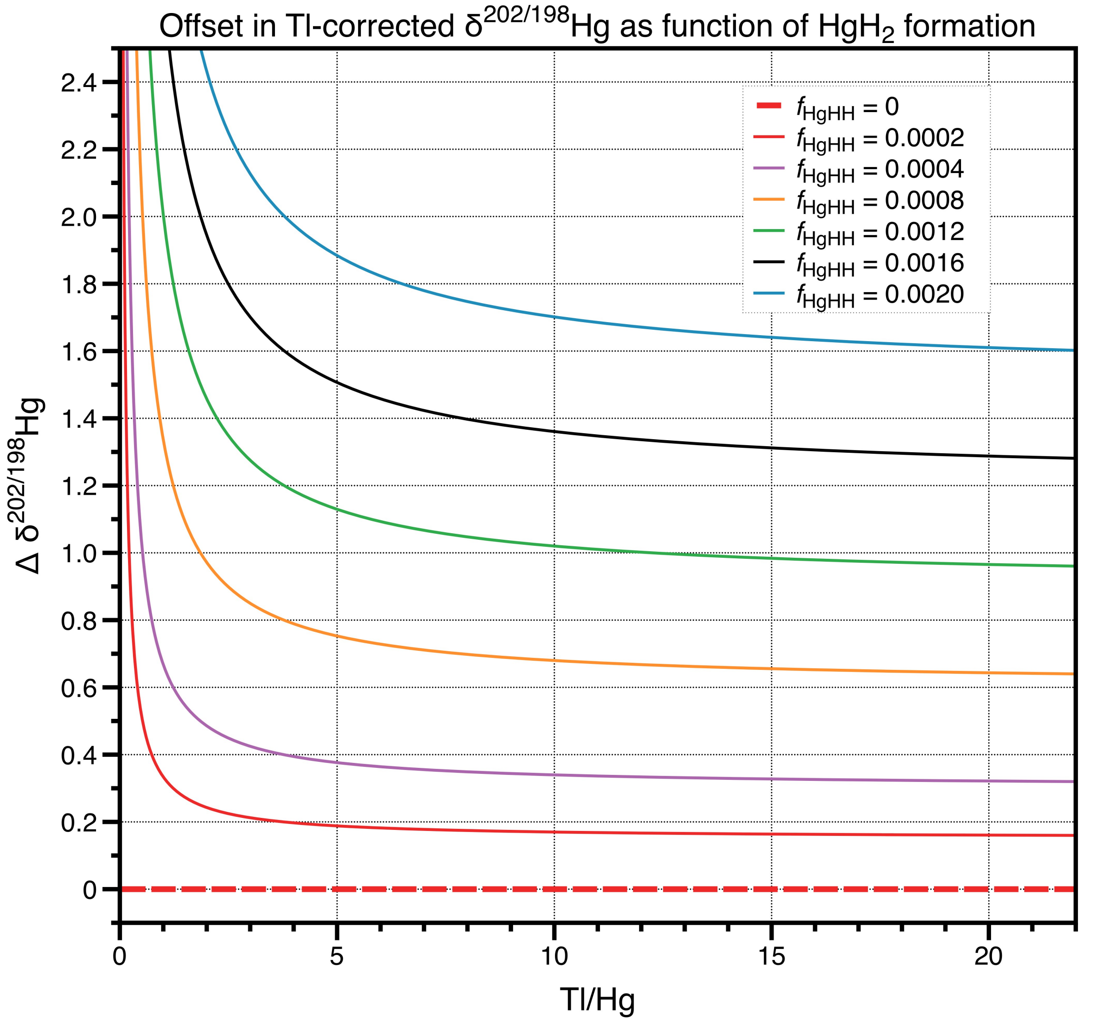

Figure 6: Measured Tl-corrected mass-dependent Hg isotope ratios (here given as $\delta^{202/198}$Hg) can be offset due to HgH_2 formation. For a given hydride formation rate, the effect is less pronounced for samples having high Tl/Hg intensity ratios, e.g. concentration of internal Tl standard is high.

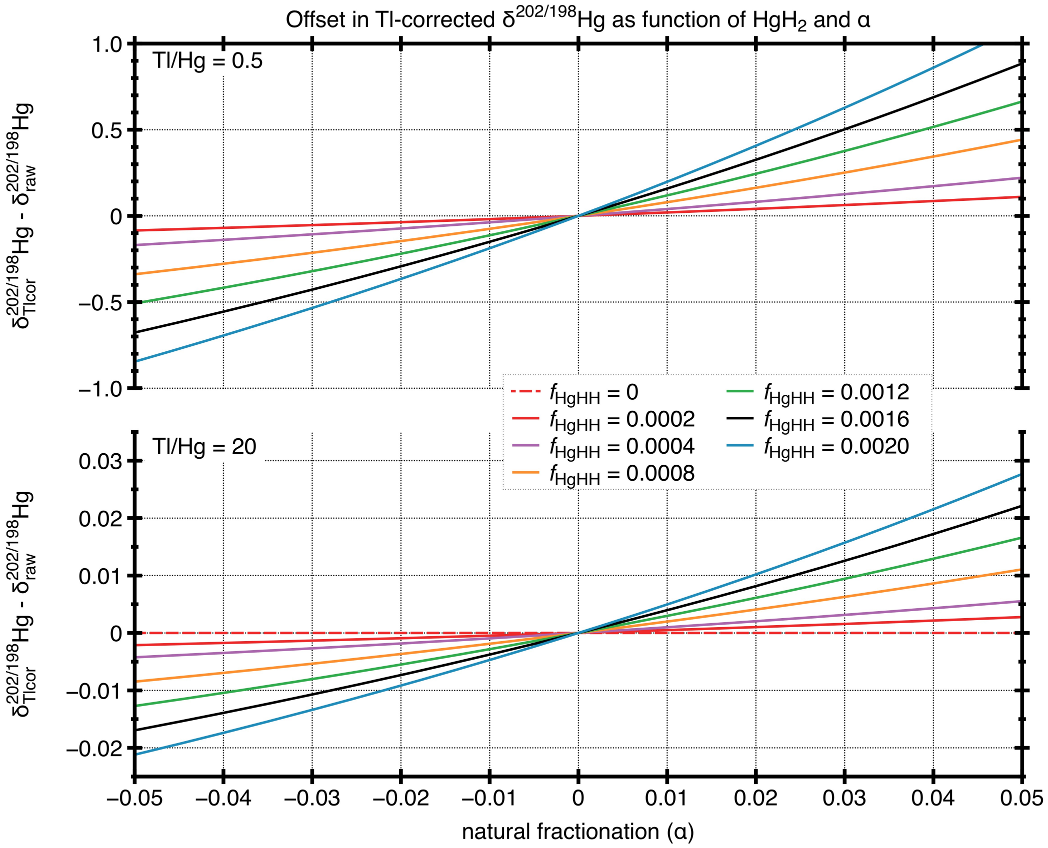

Figure 7: Mercury-hydride formation shifts the relative isotope abundances and natural isotope fractionation can amplify or inhibit the effect. A moderate natural isotope fractionation of α = 0.02 in a sample means the measured and Tl corrected mass-dependent δ^{202}Hg ratio will be about +0.4‰ offset from the true value for a hydride formation rate of 0.2% and a Tl/Hg ratio of 0.5. When hydride formation rates are as high as 0.2%, increasing the Tl/Hg ratio to 20 will reduce this artificial bias to +0.01‰.

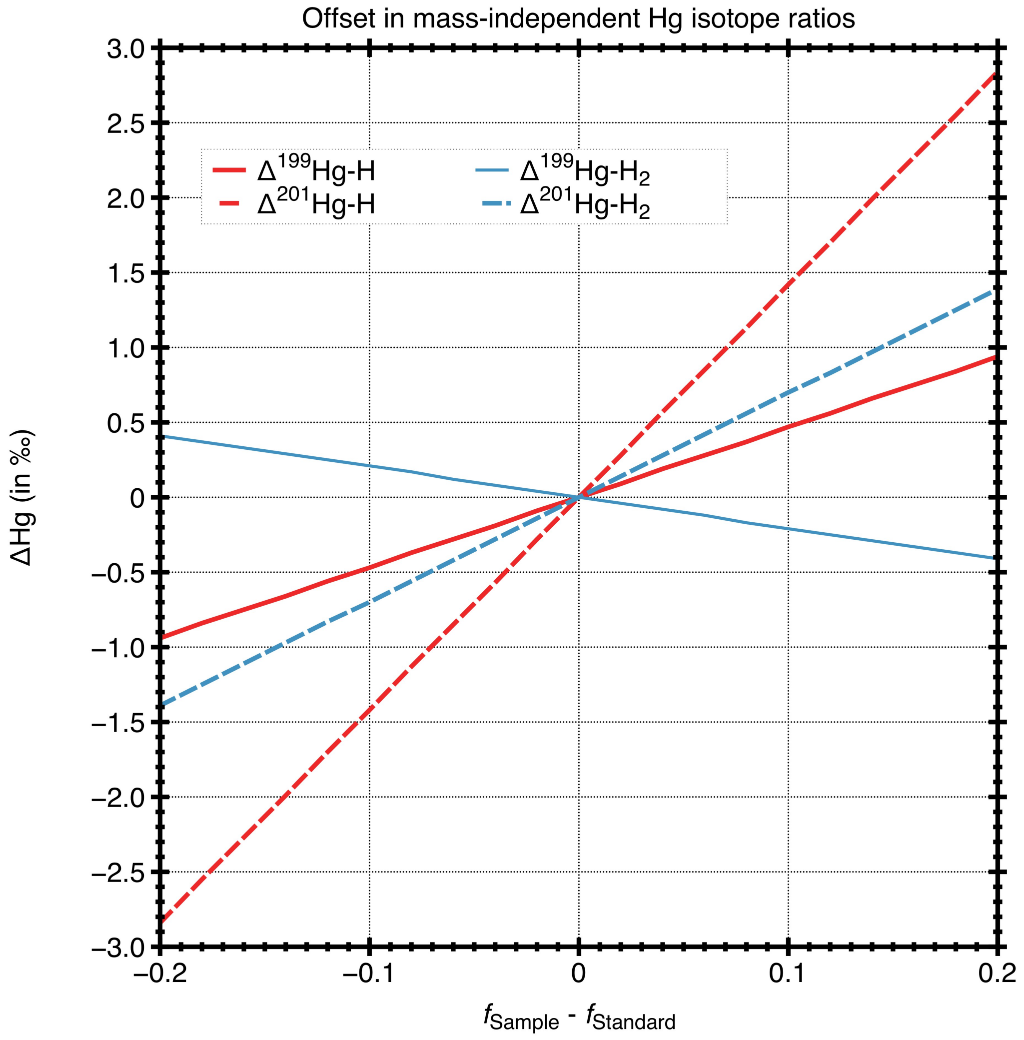

Figure 8: Mass-independent Hg isotope ratios are very sensitive to variable hydride formation rates and significant mass-independent effects are produced when hydride formation rates between samples and bracketing standards varies slightly. Note, the formation of mono-hydrides produces the same directional offsets in Δ^{199}Hg and Δ^{201}Hg for a given difference in formation rates (red lines). If predominantly di-hydrides form (blue lines), offsets in Δ^{199}Hg and Δ^{201}Hg have opposite signs.