# SUPPLEMENTARY INFORMATION

## 1. Equation of the expected time lag range

$$\tau = RC \qquad (1)$$

$$\tau + \Delta\tau = (R + \Delta R)(C + \Delta C) \Rightarrow$$

$$\tau + \Delta\tau = RC + R\Delta C + C\Delta R + \Delta R\Delta C \qquad (2)$$

$$(2)/(1) \Rightarrow \frac{\Delta\tau}{\tau} = \frac{\Delta C}{C} + \frac{\Delta R}{R} + \underbrace{\frac{\Delta R}{R} \times \frac{\Delta C}{C}}_{\text{negligible}} \Rightarrow$$

$$\frac{\Delta\tau}{\tau} = \frac{\Delta C}{C} + \frac{\Delta R}{R} \qquad (3)$$

## 2. d-DIHEN Neptune MC-ICPMS

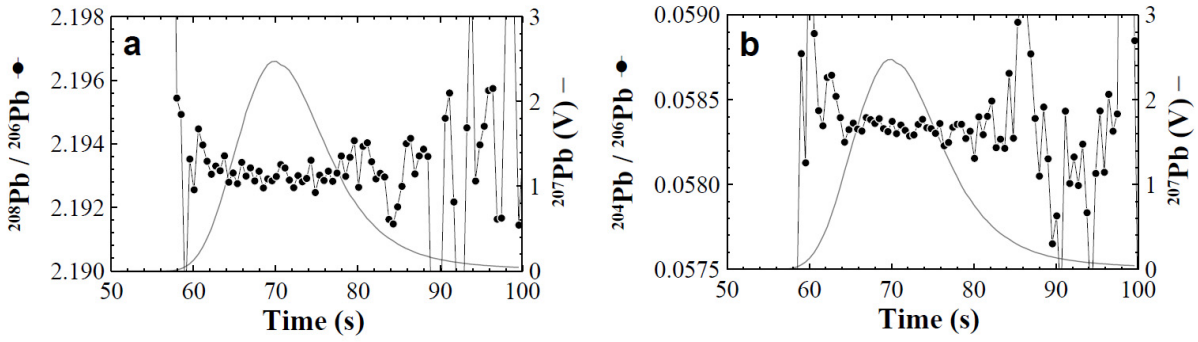


**Figure 1.** Lead transient signals with flow injection and d-DIHEN on a Neptune MC-ICPMS. As can be seen the $^{208}$Pb/$^{206}$Pb (a) and the $^{204}$Pb/$^{206}$Pb (b) isotope ratios do not show isotope ratio drift.

## 3. Relative Standard Deviation-based model (RSD model)

Based on the relative standard deviation equation for the $V_a^{ti}/V_b^{ti}$ isotope ratios and by replacing $V_a^{ti}$ by $V_a(t_i+\Delta t)$ we obtain the *Relative Standard Deviation-based* model (*RSD* model):

$$RSD(\Delta t)=\left(\sqrt{\frac{\sum_{i=1}^{n}\left(\frac{V_a(t_i+\Delta t)}{V_b^{ti}}-\frac{\sum_{i=1}^{n}\frac{V_a(t_i+\Delta t)}{V_b^{ti}}}{n}\right)^2}{n-1}}\Bigg/\frac{\sum_{i=1}^{n}\frac{V_a(t_i+\Delta t)}{V_b^{ti}}}{n}\right)\times 100 \qquad (4)$$

A comparison between the *Slope* and the *RSD* model is given in the GC-MC-ICPMS Supplementary Information section 4 (Figure 2).

## 4. Nu Plasma GC-MC-ICPMS

### 4.1 GC-MC-ICPMS $\Delta t_{min}$ values

$\Delta t_{min}$ values for the GC-MC-ICPMS sample injections were calculated using the *Slope* and the *RSD* models. Both sets of results were found to be in good agreement, with $\Delta t_{min}$ relative differences between the two models of <0.2%, <1% and <6% for $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{204}Pb/^{206}Pb$ isotope ratios respectively.

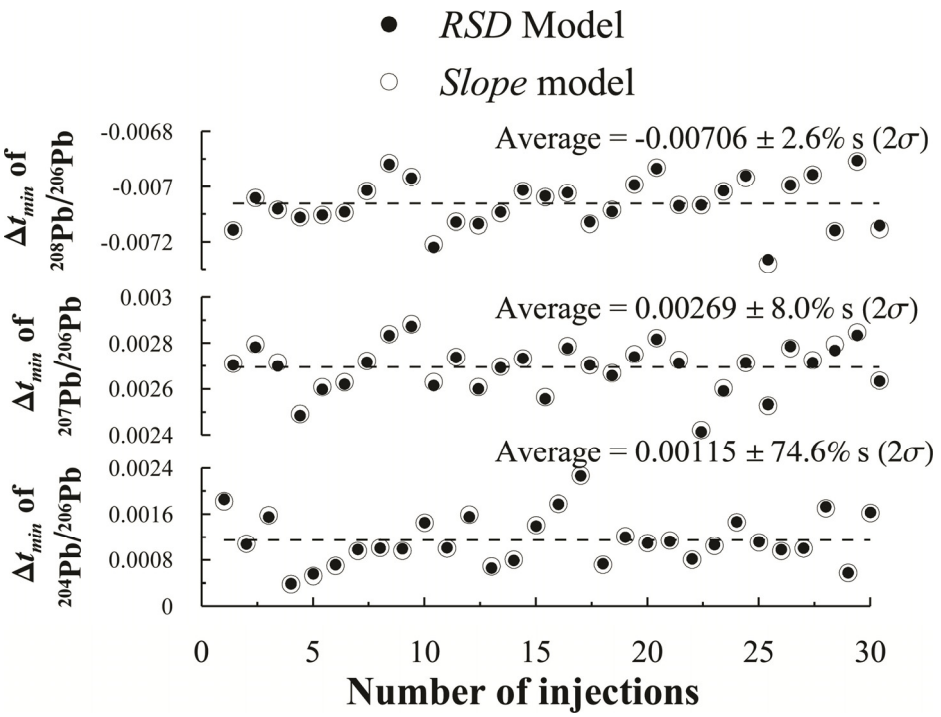


**Figure 2.** $\Delta t_{min}$ values for the *Slope* and *RSD* models for the $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{204}Pb/^{206}Pb$ isotope ratios.

4.2 Deviation of the corrected isotope ratios from the Exponential Mass Fractionation Law

In order to highlight small deviations of the corrected isotope ratios from the EMFL, a 3D view of $^{207}Pb/^{206}Pb$ - $^{208}Pb/^{206}Pb$ isotope ratios against $^{208}Pb$ signal was performed (Figure 3). The Z-axis corresponds to $^{208}Pb$ continuously changing signal intensity, which significantly influences the counting statistics (Poisson law) and therefore the isotope ratio precision and the gray surface the Exponential Mass Fractionation Law (EMFL). As can be seen the uncorrected drift data (blue points) show significant deviations from the EMFL due to the time lag between the Faraday-amplifier systems. In contrast, the drift corrected data (red points) fit much better with the EMFL. However, for $^{208}Pb$ intensities higher than 10 V, the drift corrected data show a slight deviation (~250 ppm) from the EMFL (right side). For intensities lower than 10 V, $^{207}Pb/^{206}Pb$ - $^{208}Pb/^{206}Pb$ ratios are randomly dispersed around the EMFL. Different fractionation laws were used (Power and Linear Laws) they displayed differences relative to the EMFL which are not distinguishable for the dispersion of our data. This isotopic deviation from the EMFL has been attributed to the superposition of the

classical mass discrimination isotope evolution (EMFL) with a non-exponential effect, the physical origin of which has not yet been identified. Unlike $^{207}Pb/^{206}Pb$ - $^{208}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$ - $^{208}Pb/^{206}Pb$ results are not conclusive, due to the large dispersion of the corrected $^{204}Pb/^{206}Pb$- $^{208}Pb/^{206}Pb$ ratios around the EMFL which may be related to the lower intensity of $^{204}Pb$ compared to other Pb isotopes.

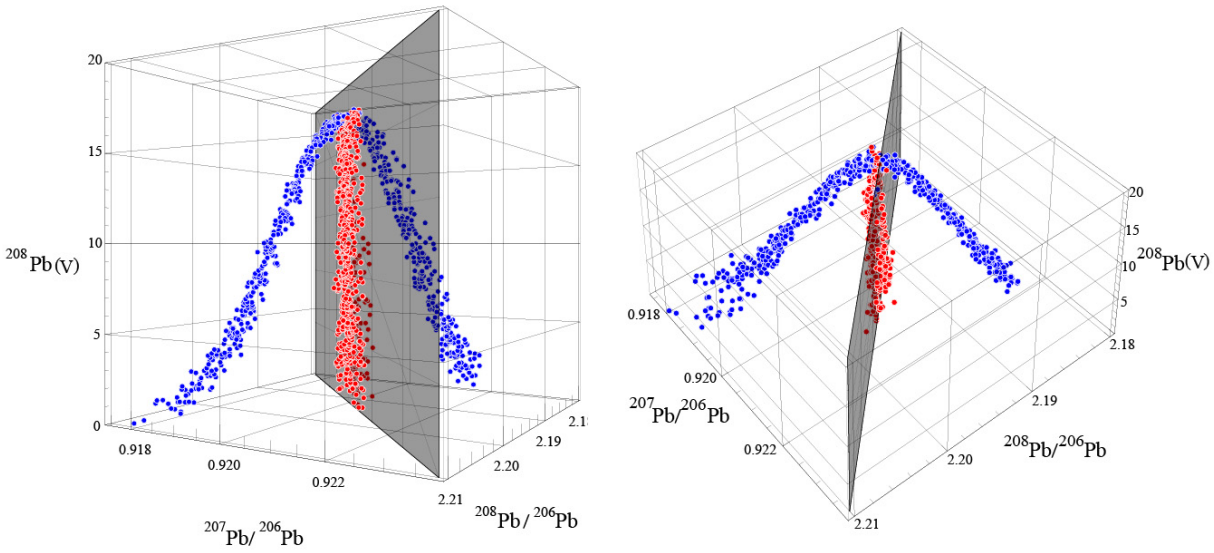


**Figure 3.** 3D view of $^{207}Pb/^{206}Pb$ - $^{208}Pb/^{206}Pb$ against $^{208}Pb$ signal intensity. The Z-axis represents $^{208}Pb$ intensities and the gray surface the Exponential Mass Fractionation Law (EMFL). As can be seen the drift uncorrected data (blue points) show significant deviations from the EMFL. In contrast, the drift corrected data (red points) fit much better with the EMFL.

## 5. Error propagation equations

According to the exponential mass fractionation law, the mass fractionation factor $\beta$ is calculated from the next equation:

$$\beta = \frac{\ln\left(\frac{R}{r}\right)}{\ln\left(\frac{M_{208}}{M_{206}}\right)} \quad (5)$$

Where $R$ and $r$ are respectively the reference and measured values of the $^{208}Pb/^{206}Pb$ isotope ratio. For the reference ratio the 2.1681 value was used and no uncertainty was considered. $M_{208}$ and $M_{206}$ are the atomic masses of $^{208}Pb$ and $^{206}Pb$ respectively.

The uncertainty $\sigma_\beta$ of the mass fractionation factor $\beta$ was calculated using the next equation:

$$\sigma_\beta = \sqrt{\left(-\frac{1}{r\ln\left(\frac{M_{208}}{M_{206}}\right)}\right)^2 \sigma_r^{\,2}} \quad (6)$$

Where $r$ and $\sigma_r$ are respectively, the measured isotope ratio $^{208}Pb/^{206}Pb$ and its uncertainty. This uncertainty was calculated using the standard deviation ($\sigma$) for the PbP method and the slope uncertainty (SE) for LR method.

The individual injection uncertainties ($\sigma_R$) were calculated by the following equation:

$$\sigma_R = \sqrt{\left(\frac{M_{207}}{M_{206}}\right)^{2\beta}\sigma_r^2 + \left[\left(\frac{M_{207}}{M_{206}}\right)^{\beta} r\ln\left(\frac{M_{207}}{M_{206}}\right)\right]^2\sigma_\beta^2 + 2\rho_{r,\beta}\left(\frac{M_{207}}{M_{206}}\right)^{\beta}\left[\left(\frac{M_{207}}{M_{206}}\right)^{\beta} r\ln\left(\frac{M_{207}}{M_{206}}\right)\right]\sigma_r\sigma_\beta} \quad (7)$$

$\rho_{r,\beta}$ is the correlation coefficient between the fractionation factor $\beta$ and the $^{207}Pb/^{206}Pb$ isotope ratio. It was calculated using the command "*Correlation*" of *Mathematica* software and can also be calculated using the function "*Correl*" *of MS EXCEL*.

Equation 7 can be easily adapted for uncertainty calculation of $^{204}Pb/^{206}Pb$ isotope ratio.