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Characterization of actinide abundances and isotopic compositions by HR-ICP-MS

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Report Summary

In this report, we present actinide isotopic and elemental data from fallout melt glass using high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). This is an analytical technique that requires minimal sample preparation. These data are directly compared to the results of high precision isotopic analyses and elemental assay by multi-collector (MC-) ICP-MS, which requires lengthy sample processing involving spiking and purifying aliquots of individual elements. The comparison shows broad overlap between the results of the two techniques. Thus, although the data obtained by HR-ICP-MS is of significantly lower precision, it is a viable method to obtain actinide elemental and isotopic data on a more rapid timeframe than traditional high-precision techniques.

Introduction

High-precision actinide isotopic and elemental analyses typically require time-consuming sample preparation prior to analysis. This is particularly true in samples with complicated matrices where actinides are trace constituents. In such cases, it is beneficial to purify the actinide of interest from the remaining sample matrix using techniques such as ion-exchange chromatography. This reduces isobaric and polyatomic interferences from affecting the measured isotope ratios and reduces matrix differences between samples and standards, which can cause changes in the instrumental mass bias. If samples are spiked with an isotopic tracer prior to chemical separation, it is possible to combine the isotopic analysis with an elemental assay. This is the preferred method to characterize the abundance and isotopic composition of actinides for a range of nuclear forensics

purposes, including the characterization of fallout melt glass from historic nuclear tests (*e.g.*, Eppich et al., 2014; Wimpenny et al., 2022).

One problem with this method is that the sample preparation processes can be time and labor intensive. Typically, elemental and isotopic data is obtained for U, Pu, Am, and Np, each of which requires a different, multi-stage purification procedure. Furthermore, the abundance of each actinide in a piece of nuclear debris can be highly variable, meaning approximate characterization of actinide abundances must be performed first to ensure an optimal sample-spike ratio. Although the payoff from this effort is a set of high-quality isotopic data, such a drawn-out analytical timeframe is not practical when rapid results are required. For this reason, we have investigated whether accurate actinide abundance and isotopic data can be obtained without performing sample purifications and without the use of an internal isotopic tracer (*i.e.*, without isotope dilution). Here, we present the results of a direct comparison between actinide data obtained by HR-ICP-MS during trace element analyses—which can occur directly following sample dissolution—and actinide data obtained by high-precision MC-ICP-MS that requires spiking and chemical purification.

Methods

Detailed description of the methods used at LLNL to obtain trace element abundance data by HR-ICP-MS and actinide isotope data by MC-ICP-MS are provided elsewhere (*e.g.*, Eppich et al., 2014; Mathew et al., 2019; Treinen et al., 2019; Wimpenny et al., 2022). Here, we focus on the methods to characterize actinide isotopic abundances by HR-ICP-MS and comparison with MC-ICP-MS data.

Sample preparation

Fallout glass samples were digested using a combination of ultrapure concentrated HNO_3, HF, and HCl. Typical sample masses are ~100mg. Once fully digested, samples were redissolved in 5ml of 6M HCl, from which sub aliquots for trace element and isotopic analysis were taken. Typically, the final stock solutions contain ~0.02g of sample per gram of solution. To prepare samples for trace element analyses requires a sub-aliquot to be weighed into a pre-cleaned Savillex vial. Typical sub-aliquot masses are <100µl, or <2% of the initial sample mass. The sub-aliquot is dried and redissolved in 5ml of internal standard solution (2% HNO_3 + 0.005M HF), which contains ~1 ng/g of In, Re, and Bi. These internal standard elements are used to monitor matrix suppression and in-run drift during the trace element analysis. The sample solution has an approximate dilution factor of 10,000×, meaning typical trace elements that are present the µg/g-level in a sample can be analyzed at the ng/g level by ICP-MS. Calibration standards were prepared alongside the samples using serial dilutions of standardized concentration solutions (Inorganic Ventures). These serial dilutions were performed using the same internal standard solution as the samples.

Elemental analyses performed by HR-ICP-MS

All elemental analyses were performed using the Thermo Scientific Element XR HR-ICP-MS at LLNL. The instrument was configured with standard 'H' sample and skimmer cones, and samples were introduced to the plasma using a 100 µl/min glass nebulizer (Glass Expansion) and dual-cyclonic quartz spray chamber. In this configuration the typical signal generated by a 1 ng/g solution of In ranges between 1-2×10^6 counts per second (cps). The Element XR has 3 detector

modes spanning a dynamic range of >9 orders of magnitude, enabling trace and major elements to be measured at the same time. It also has a changeable entrance and exit slit system, which enables measurements to be performed at low, medium or high resolutions (m/Δm = 300, 4000, or 10,000 respectively. At higher resolution the entrance and exit slits narrow, meaning it is easier to resolve interferences from the isotope of interest. For example, high resolution mode can be used to resolve ^{39}K from $^{38}Ar^{1}H$ and medium resolution can be used to resolve ^{56}Fe from $^{40}Ar^{16}O$.

Prior to sample analysis, the instrument is tuned to enhance sensitivity and lower oxide production to <10%. The peak shapes in MR and HR are also refined to ensure optimal resolving power is achieved. In addition to a standard selection of major and trace elements, the method also includes a suite of actinide isotopes including ^{234}U, ^{235}U, ^{236}U, ^{237}Np, ^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Pu ($+^{241}Am$), and ^{242}Pu. All actinide isotopes are analyzed in LR mode. A subset of isotopes including ^{235}U and ^{238}U are also analyzed in MR mode. Raw data is exported and reduced offline. Corrections are made for shifts in the intensity of the internal standard and instrument blank. The calibration standards contain uranium with a depleted ^{235}U content and unknown minor isotope abundances. They also contain no plutonium, americium, or neptunium. To convert intensities into concentrations we assume that ^{238}U is a good proxy for the behavior of the other actinides in the mass spectrometer. Thus, a calibration curve is created between the measured counts of ^{238}U and known ^{238}U concentrations in the standard solutions. The slope of the curve reflects the response of the detector to a solution with a known concentration. This slope, or calibration value, is then applied to all other actinide isotopes to obtain final concentrations. The uncertainty of the slope is propagated into the final uncertainties. Quality control checks are performed using USGS rock standards to assess the accuracy of major and trace element abundances, which typically agree with reference values to within 10%.

Results

Concentration measurements

Direct assessment of the accuracy of HR-ICP-MS concentration measurements can be made by comparing the data with isotope dilution measurements of the same samples, which are assumed correct. Results are shown in Fig. 1 and 2.

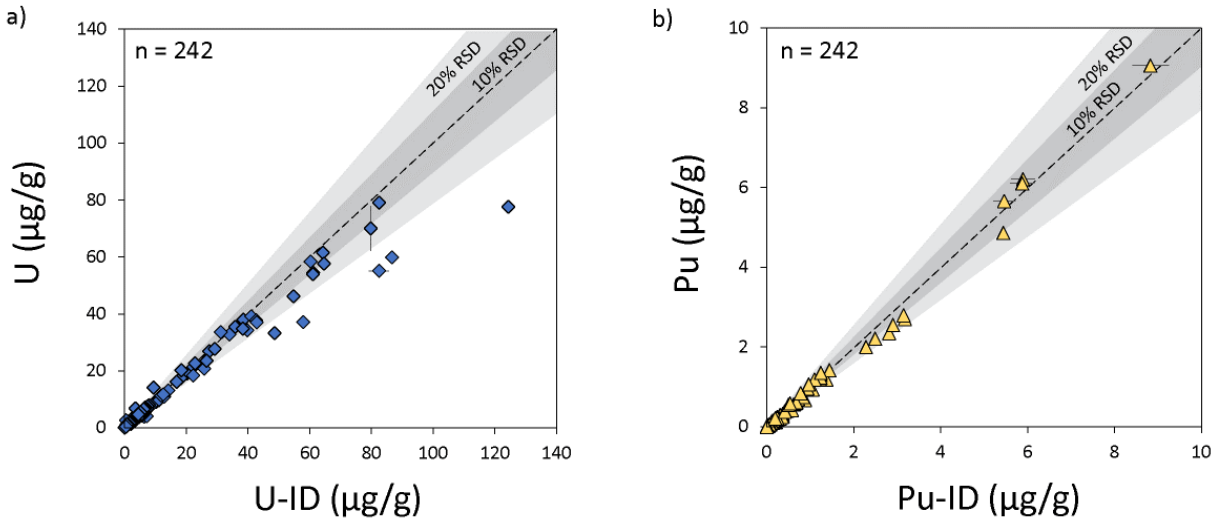

Fig. 1 – Comparison between U and Pu concentrations measured during trace element analyses (y-axis) and concentrations obtained using isotope dilution (x-axis). Equivalence is represented by the dashed line. All uncertainties are 2σ.

In general, there is good agreement between the U and Pu concentrations measured by HR-ICP-MS and concentrations obtained by isotope dilution MC-ICP-MS (Fig. 1). For both elements, the HR-ICP-MS data tend to be slightly lower, with typical offsets of ~10% compared to the isotope dilution data. This is most evident for samples with U concentrations >40 µg/g (Fig. 1a). Of the two elements, Pu data obtained by HR-ICP-MS are more consistent with the isotope dilution data, despite typical concentrations that are an order of magnitude lower than U.

Despite typical concentrations in the pg/g to ng/g range, it is also possible to obtain data for ^{237}Np and, by indirect methods, for ^{241}Am (Fig. 2). For both elements there is good agreement between HR-ICP-MS and isotope dilution data. Here, we note that ^{241}Am cannot be measured by direct methods during a trace element analysis. This is because both Am and Pu are present in the bulk sample aliquot and ^{241}Pu cannot be resolved from ^{241}Am using ICP-MS. This means that the mass-241 data is a combined signal from both isotopes. Instead, the ^{241}Am abundance can be calculated after characterization of the Pu isotopic composition. This requires the measured ^{241}(Pu + Am)/^{239}Pu ratio, combined with the concentrations of ^{239}Pu and ^{241}Pu in the sample that derive from the isotope dilution analysis.

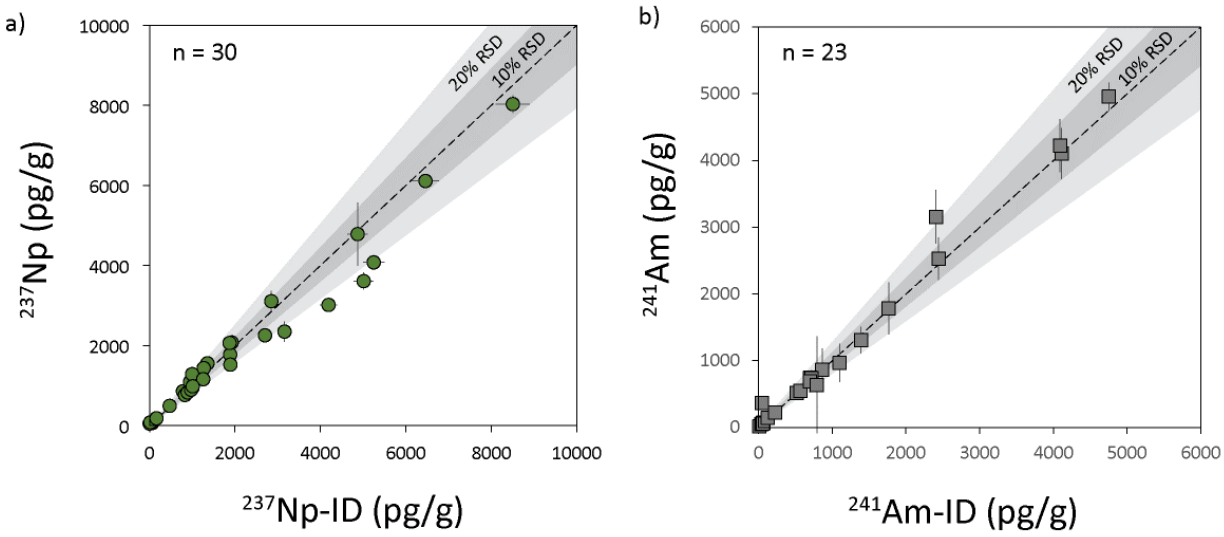

Fig. 2 – Comparison between ^{237}Np and ^{241}Am concentrations measured during trace element analyses (y-axis) and concentrations obtained by isotope dilution (x-axis). The ^{241}Am data is back calculated using the measured ^{241}(Am + Pu)/^{239}Pu and the concentrations of ^{239}Pu and ^{241}Pu that derive from the Pu ID analysis. Equivalence is represented by the dashed line. All uncertainties are 2σ.

Isotope ratio data

The isotope ratio data obtained by HR-ICP-MS is directly compared with MC-ICP-MS data for U and Pu in Fig. 3 and 4. For uranium, ^{235}U/^{238}U data was obtained in both low and medium resolution modes on the HR-ICP-MS (Fig. 3a and b). In both cases, there are clear correlations between their isotopic compositions and those obtained by MC-ICP-MS. The ^{235}U/^{238}U data

measured in low resolution is consistently ~20% lower than the MC-ICP-MS data, whereas the medium resolution data is consistently 5-10% higher. The minor isotope ratios ($^{234}U/^{238}U$ and $^{236}U/^{238}U$) obtained by HR-ICP-MS also correlate with the MC-ICP-MS data. These data were obtained in low resolution mode and the $^{234}U/^{238}U$ data is also offset to lower values than the MC-ICP-MS data by 10-20% (Fig. 3c). In contrast, the $^{236}U/^{238}U$ data lie directly on the 1 to 1 line (Fig. 3d).

The plutonium isotope data obtained using the HR-ICP-MS agrees well with the MC-ICP-MS data, with the majority of data points lying on the 1:1 line (Fig. 4). Here, we note that the uncertainties associated with $^{240}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ measured by HR-ICP-MS can be significant, often due to relatively low Pu intensities in some samples.

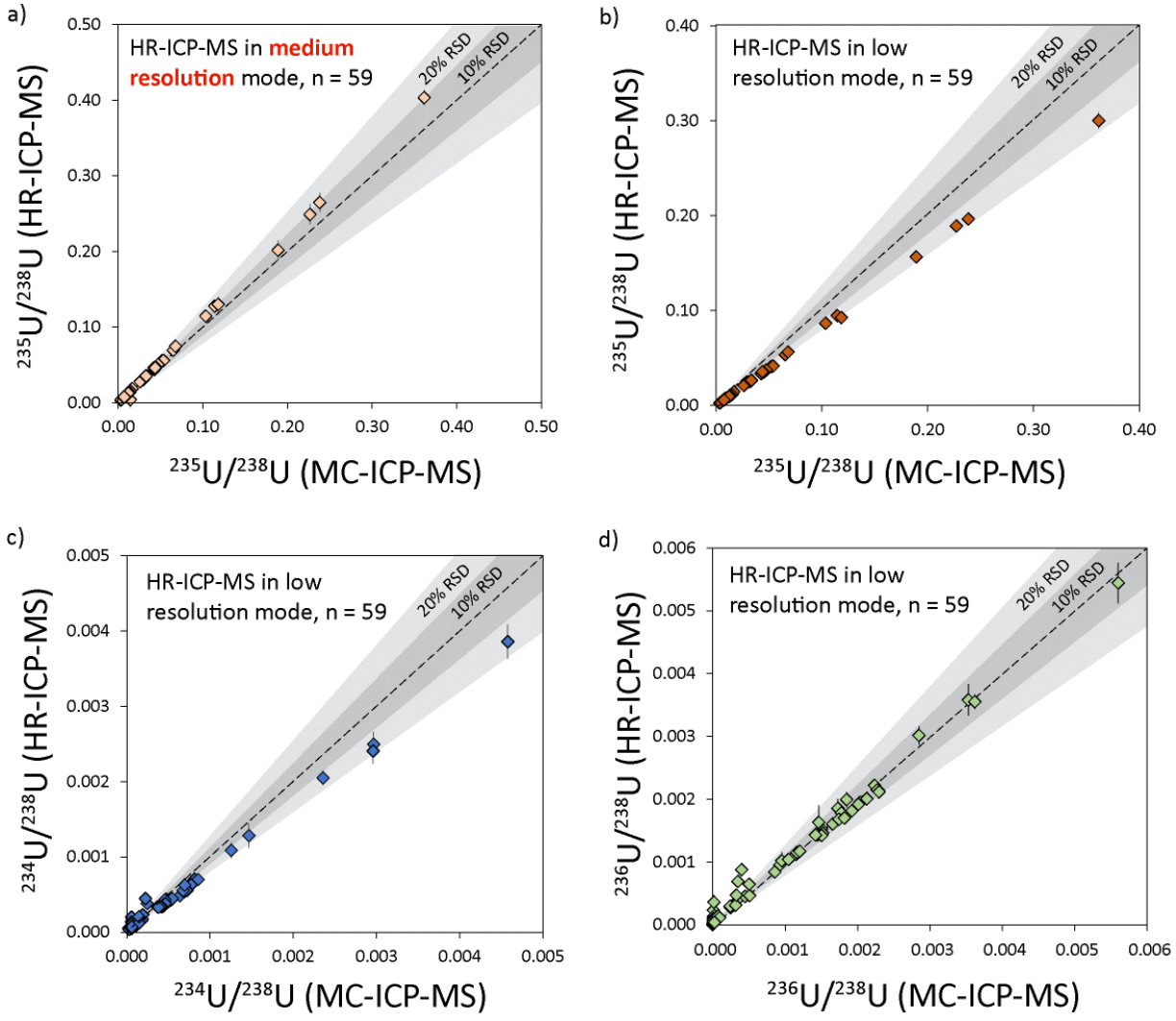

Fig. 3 – Comparison between the U isotopic composition measured by HR-ICP-MS (bulk sample) and MC-ICP-MS (purified uranium).

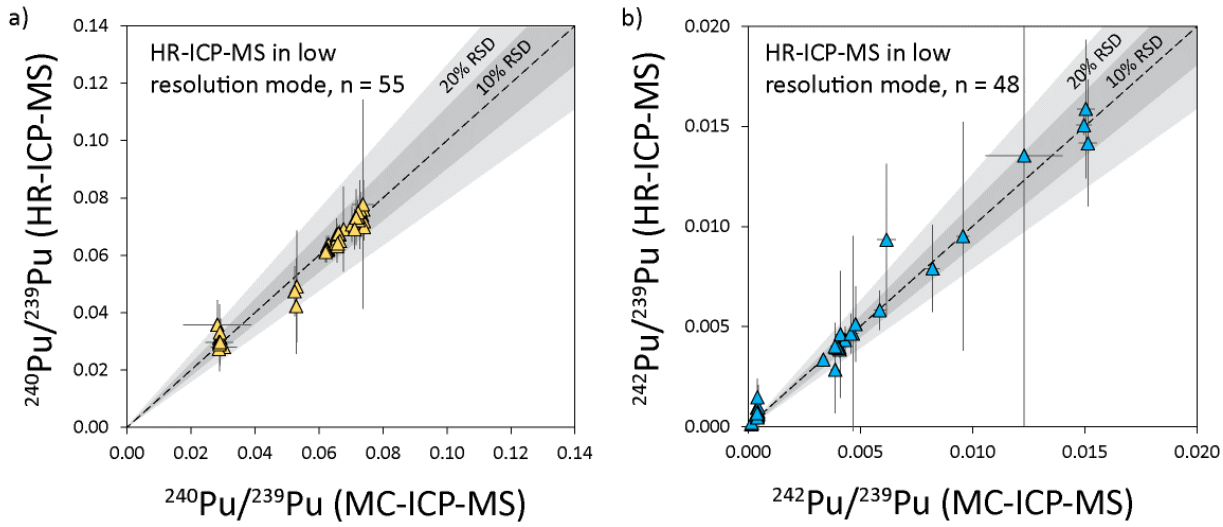

Fig. 4 - Comparison between the Pu isotopic composition measured by HR-ICP-MS (bulk sample) and MC-ICP-MS (purified plutonium).

Discussion

Concentration measurements

The concentrations of U, Pu, Np, and Am obtained by HR-ICP-MS are generally consistent with the data obtained by isotope dilution MC-ICP-MS (Fig 3). In Fig. 5, we plot the %-offset in the HR-ICP-MS data as a function of concentration (using the isotope dilution data as the assumed true values). For each element the data cluster around the 0% offset line but in each case there is a tendency for the HR-ICP-MS data to be slightly lower than concentrations obtained by isotope dilution. This could reflect a small mass bias effect between the samples and calibration standards, which have very different matrices. Nevertheless, on average the offsets in the data produced by HR-ICP-MS are relatively minor (<10%), which is consistent with the level of accuracy that is expected for trace element measurements. For U and Pu there are a subset of samples with very low concentrations that exhibit significant relative offsets in the HR-ICP-MS data (50-100%). Due to their low abundances, it is likely that these samples suffer to a larger extent from artifacts associated with blank or polyatomic interferences as the count rates approach the detector baseline. Finally, although ^{241}Am data is collected during a standard HR-ICP-MS analysis, the absolute abundance of ^{241}Am cannot be ascertained until Pu isotopics are obtained. Thus, it would not be possible to produce ^{241}Am data by HR-ICP-MS on the same timeframe as the other actinides. However, having a secondary method to calculate the ^{241}Am abundance is a useful quality control check on the isotope dilution method; for example, to identify an error in spiking or weighing during preparation of the purified Am aliquot.

Ultimately, these data confirm that standard trace element analysis by HR-ICP-MS can obtain actinide abundances in fallout that are fully consistent with data obtained by isotope dilution, albeit at a lower precision. The use of ^{238}U as a calibrant for the other actinide isotopes produces accurate concentration data, confirming the assumption that U behaves similarly to Np, Pu, and Am during ionization in the plasma and extraction into the ICP-MS. Thus, the use of specialized calibration

solutions containing species such as ^{239}Pu or ^{237}Np would be unlikely to greatly improve the final data obtained by HR-ICP-MS until accuracy of these analyses can be improved beyond the 10% level.

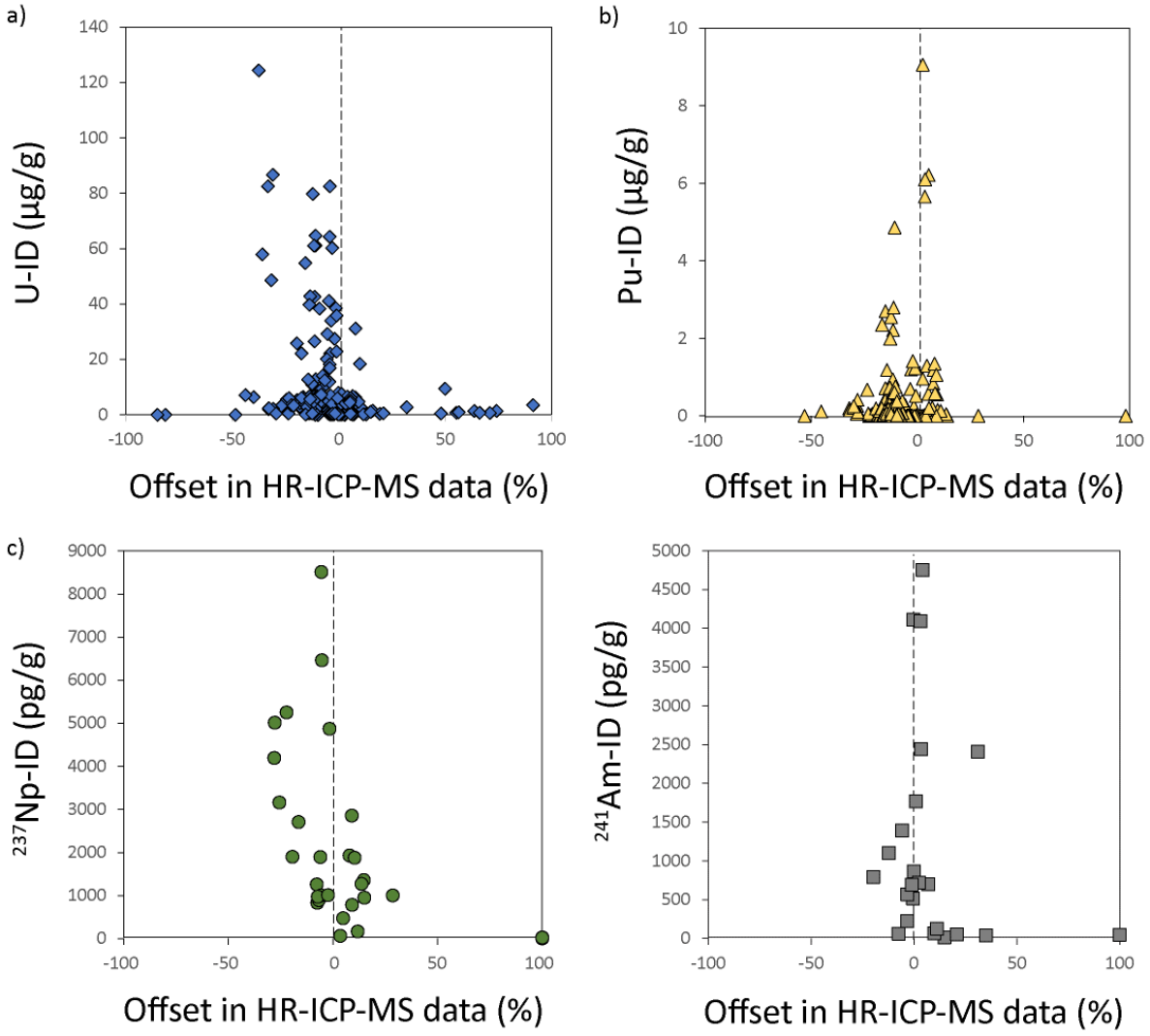

Fig. 5 – Plotting the offset in the U, Pu, Np and Am concentrations obtained by HR-ICP-MS and isotope dilution (x-axis) as a function of the 'true' concentration obtained by isotope dilution analyses (y-axis)

Isotopic analyses

The U and Pu isotopic compositions measured during trace element analyses by HR-ICP-MS correlate with the data obtained by MC-ICP-MS. This means that the HR-ICP-MS data can potentially provide important information about the isotopic composition of an unknown sample without the requirement for time intensive sample processing. The caveats are that i) the data is of relatively low precision compared to MC-ICP-MS and ii) some isotope ratios (*e.g.*, ^{235}U/^{238}U and ^{234}U/^{238}U) are systematically offset from the MC-ICP-MS data. The importance of these caveats

depends on the level of accuracy that can be tolerated for data obtained on a rapid timeframe and/or whether systematic offsets in the HR-ICP-MS data can be satisfactorily corrected. To this latter point, it is important to consider whether the offset-factor between HR-ICP-MS data and MC-ICP-MS data is robust and if the cause of the offset can be constrained and potentially corrected during future analytical development.

The $^{235}U/^{238}U$ and $^{234}U/^{238}U$ ratios measured by HR-ICP-MS are offset by ~20% from the known ratios measured by MC-ICP-MS (Fig. 3b). For the $^{235}U/^{238}U$ data measured in low resolution, the magnitude of this offset is remarkably consistent, with an average value of -19.3 ± 4.2% (2s, n = 59). In contrast, the $^{235}U/^{238}U$ ratios measured in medium resolution are closer to the MC-ICP-MS data, but the degree of offset is more variable (+4.7 ± 21%), This greater degree of scatter is likely caused by lower count rates. The difference in the $^{235}U/^{238}U$ ratio produced in low- and medium-resolution modes most likely reflects the presence of interfering species at the uranium mass range. These interfering species are removed, to some extent, by using a higher resolving power (m/Δm) of ~4000 at medium resolution. The identification of such species is beyond the scope of the current study. In theory, polyatomic species such as $^{195}Pt^{40}Ar$, $^{16}O^{16}O^{208}Pb$ and $^{1}H^{1}H^{28}Si^{208}Pb$ could cause analytical artifacts to be present at the uranium and plutonium mass range. The simplest explanation for the negative offsets in $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios measured by HR-ICP-MS is the presence of an interference on ^{238}U. However, it is difficult to reconcile why this would result in perturbations in the $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios and leave the $^{236}U/^{238}U$ ratios unaffected.

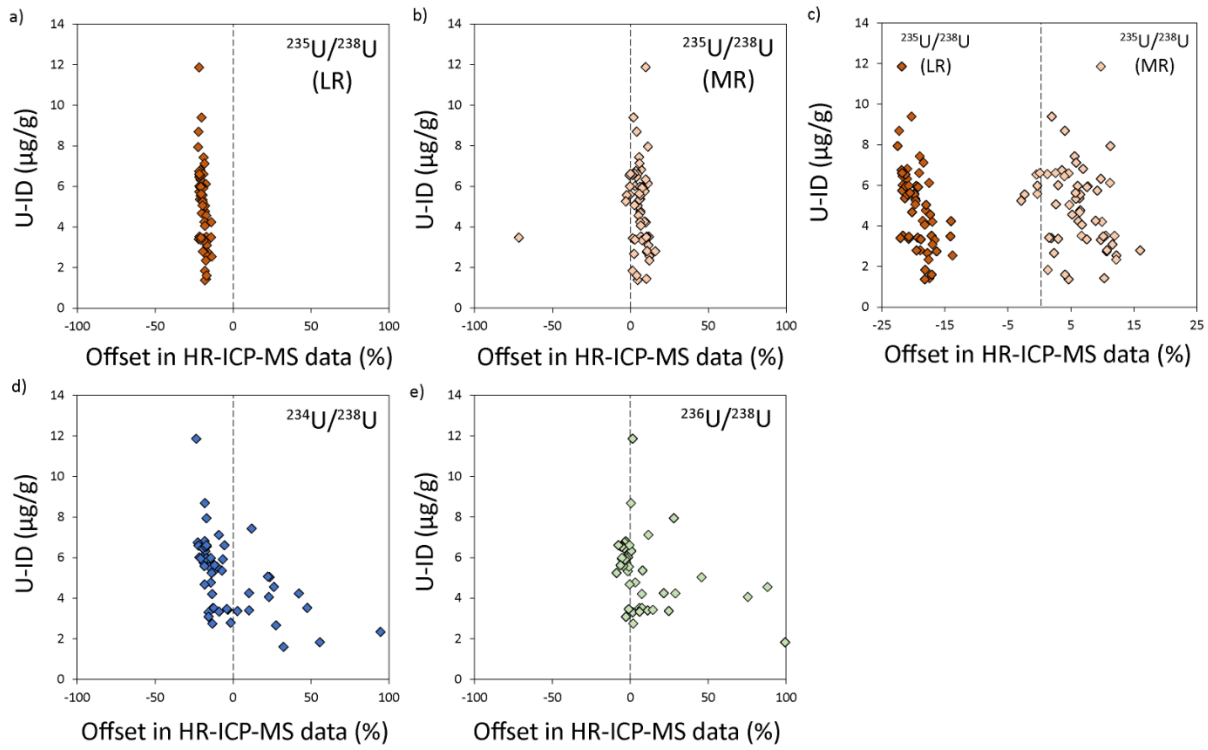

Fig. 6 - Plotting the offset in the U isotope ratios obtained by HR-ICP-MS and MC-ICP-MS (x-axis) as a function of the U concentration (y-axis). The $^{235}U/^{238}U$ data from low resolution measurements are plotted in (a), medium resolution measurements in (b) and a zoomed in scale is provided in (c) to better observe the relationship between U concentration and offset in the ratio.

To investigate further, we have plotted the offset in the U isotopic data obtained by HR-ICP-MS as a function of U concentration (Fig 6). The offset in the $^{23x}/^{238}U$ ratio (where x = ^{234}U, ^{235}U, or ^{236}U) measured by HR-ICP-MS changes with U concentration, consistent with the presence of minor interfering species that only become important when U count rates are very low. These trends are more apparent for $^{234}U/^{238}U$ and $^{236}U/^{238}U$ where relative offsets in the HR-ICP-MS data can approach 80-100%, likely because the intensities of ^{234}U and ^{236}U are approaching baseline values. The $^{235}U/^{238}U$ ratio is less dependent on the U concentration, as ^{235}U and ^{238}U are higher abundance isotopes that are more easily resolvable from instrumental backgrounds. Even so, a weak correlation exists between the $^{235}U/^{238}U$ ratio and U concentration (particularly at low resolution), with the relative offset in the $^{235}U/^{238}U$ ratio changing by 5-10% with decreasing U concentration (Fig. 6c). The combination of a major shift in the $^{235}U/^{238}U$ ratio (~20%) combined with a smaller shift in ratio that is concentration dependent indicates that the uranium isotope ratios measured by HR-ICP-MS are affected by a variety of polyatomic species and/or addition of uranium blank during sample preparation. These combined effects are likely to be difficult to eradicate or fully correct. Such problems are not surprising given that the samples have complicated silicate matrices including elements such as Si, REE's, and Pb that can form potentially problematic polyatomic species. Furthermore, trace element aliquots are usually relatively small (<1mg of dissolved solid) and the U in the sample can have non-natural isotopic compositions that are relatively easy to perturb by addition of blank with a distinctive isotopic composition. The addition of U blank could explain the perturbation in the $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios, assuming the blank had lower $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios than the samples. If that blank had a natural-like U composition it would not contain any ^{236}U, hence could explain why the $^{236}U/^{238}U$ ratios measured by HR-ICP-MS are so similar to values obtained by MC-ICP-MS, in contrast to ^{234}U and ^{235}U (Fig. 6e). A problem with this hypothesis is that the addition of U-blank to sample solutions cannot explain why the $^{235}U/^{238}U$ ratios measured by HR-ICP-MS in low and medium resolutions are so different. Thus, the causes of U isotope discrepancies in the HR-ICP-MS data cannot currently be unambiguously identified.

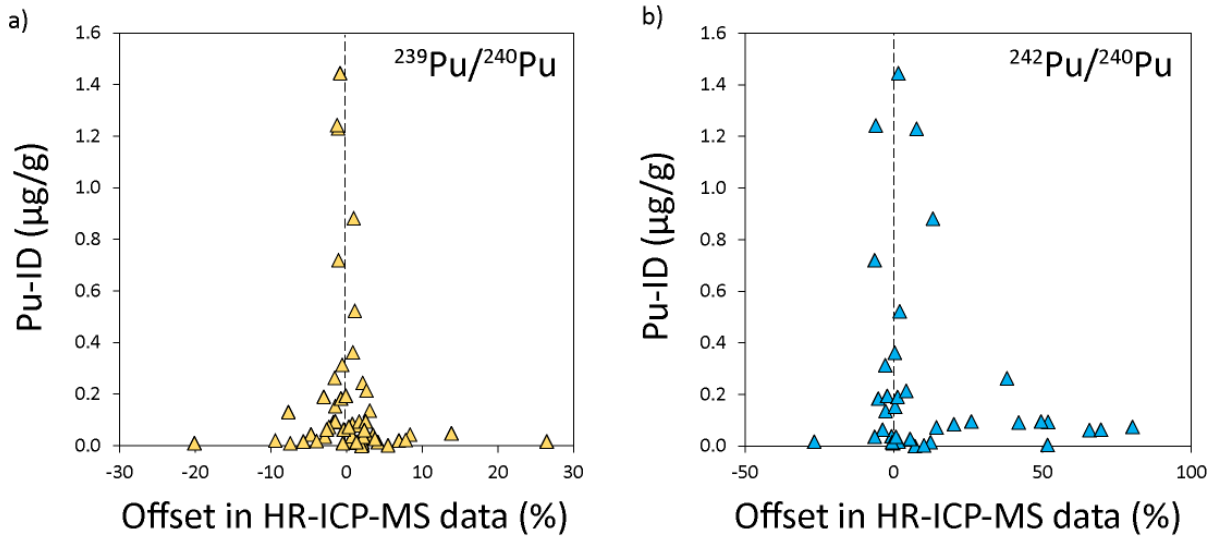

Fig. 7 - Plotting the offset in the Pu isotope ratios obtained by HR-ICP-MS and MC-ICP-MS (x-axis) as a function of the Pu concentration (y-axis)

The Pu isotopic data obtained by HR-ICP-MS is plotted as a function of Pu concentration in Fig. 7. Unlike U, the majority of Pu data obtained by HR-ICP-MS matches data obtained by MC-ICP-MS. Relative offsets in the $^{239}Pu/^{240}Pu$ and $^{242}Pu/^{240}Pu$ ratios increase in samples with lower Pu concentrations, similar to observations for U. However, no broader trends exist between the offset in isotopic composition and Pu concentration, suggesting that Pu is largely insensitive to the factors affecting the isotopic composition of U measured by HR-ICP-MS. Also, plutonium is not present in lab reagents or labware used during sample processing and is less likely to be present as a contaminant phase in sample preparation areas (compared to U) so blank addition may be less important for the HR-ICP-MS measurements.

In summary, although we cannot constrain the cause of discrepancies between U isotope data obtained by HR-ICP-MS and MC-ICP-MS the correlations between datasets mean that the HR-ICP-MS data may still provide useful information on a rapid timeframe. Our comparison demonstrates that there is good overlap between $^{236}U/^{238}U$, $^{239}Pu/^{240}Pu$, and $^{242}Pu/^{239}Pu$ data obtained by the two techniques, although care must be taken if the intensities of U and Pu isotopes approach the instrumental background levels. The most accurate $^{235}U/^{238}U$ data would be generated by applying a ~20% correction to ratios measured by HR-ICP-MS in low resolution, although consideration of the U concentration is required (Fig. 6c). The $^{234}U/^{238}U$ data is far less well constrained due to the low abundance of ^{234}U, with an average offset from the MC-ICP-MS data of -5.6 ± 44%. Due to this degree of scatter, it could be detrimental to apply a correction factor to the final $^{234}U/^{238}U$ ratio. Instead, it may be better to acknowledge that the data is of limited quality, only being accurate to within 40-50%. We caution that these correction factors/offsets are likely to be specific to individual ICP-MS instruments and/or the method of sample processing and thus would need to be well characterized if this method of correction is established in another laboratory or with different materials (*e.g.*, non-silicate). Ultimately, such correction factors may be unnecessary, depending on the degree of accuracy that is required for such rapidly attained isotopic data.

Importantly, these HR-ICP-MS data were part of an analysis protocol that aims to collect useful data for elements ranging from sub parts-per-million to weight percent in samples. The routine could be—but has not yet been—optimized for actinide collection. Optimization for actinides using the HR-ICP-MS would require significant dedicated research and development.

Conclusion

Actinide abundance and isotopic composition data obtained during trace element analyses using HR-ICP-MS correlate with data obtained by isotope dilution after sample purification and analysis by MC-ICP-MS. Although the data are of lower precision and isotopic data can be affected by interferences and/or blank addition the correlations indicate that useful information about actinide isotope systematics can be obtained rapidly with minimal sample processing in samples with complicated silicate matrices. This could be highly beneficial in circumstances where analytical data is required on a condensed timeframe.

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