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A novel fusion bead procedure for nuclear forensics employing synthetic enstatite to dissolve uraniferous and other challenging materials prior to LA-ICP-MS

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Keywords

Nuclear forensics, Laser ablation ICP-MS; flux-free enstatitic fusion; chondrite normalised lanthanide patterns; REE; uranium ore concentrates

Highlights

1. Rapid production of homogeneous flux-free syn-enstatitic glass beads.
2. Flux-free beads of high U samples reduce matrix effects and aid laser coupling in LA-ICP-MS.
3. Accurate REE patterns for international geochemical reference materials, UOCs and Mn nodules for samples sizes down to 1.5 mg.

Abstract

There is an increasing demand for rapid and effective analytical tools to support nuclear forensic investigations of seized or suspect materials. Some methods are simply adapted from other scientific disciplines and can effectively be used to rapidly prepare complex materials for subsequent analysis. A novel sample fusion method is developed, tested and validated to produce homogeneous, flux-free glass beads of geochemical reference materials (GRMs), uranium ores, and uranium ore concentrates (UOC) prior to the analysis of 14 rare earth elements (REE) via LA-ICP-MS. The novelty of the procedure is the production of glass beads using 9 parts high purity synthetic enstatite ($MgSiO_3$) as the glass former with 1 part of sample (sample mass ~1.5 mg). The beads are rapidly prepared (~10 minutes overall time) by fusing the blended mixture on an iridium strip resistance heater in an argon-purged chamber. Many elements can be measured in the glass bead but the rare earth group in particular are a valuable series in nuclear forensic studies and are well-determined using LA-ICP-MS. The REE data obtained from the GRMs, presented as chondrite normalised patterns, are in very good agreement with consensus patterns. The UOCs have comparable patterns to solution ICP-MS methods and published data. The attractions of the current development are its conservation of sample, speed of preparation and suitability for microbeam analysis all of which are favourable for nuclear forensics practitioners and geochemists requiring REE patterns from scarce or valuable samples.

1. Introduction

Nuclear forensics as a technical discipline has emerged significantly over the last two decades and uses a broad array of advanced analytical procedures to characterise seized or suspect nuclear and related materials [1–8]. The insights gained from such data are used to control suspected trafficking activities, to deter nuclear terrorism and to verify that international nuclear treaties are being upheld. There is an ever-present international threat that nuclear or other radioactive material could be acquired for use in criminal acts. This requires vigilance from the authorities and demands that the radioanalytical community continually develop, refine and improve a range of robust and rapid analytical methods to support the specialist investigative and law enforcement agencies.

Micro-analytical fusion-with-flux methods: Many seized suspect materials requiring investigation will be sparingly soluble or insoluble in mineral acids and are often heterogeneous. In these cases more specialised fusion methods could be more suitable for producing representative glassy and homogeneous materials for analysis. Analytical approaches for trace elemental analyses such as XRF, ICP-OES and ICP-MS, despite having their individual advantages, typically require sample masses >100 mg (ICP-OES and –MS) or >500 mg (XRF) to reduce detection limits. Borate fusion techniques (often lithium tetraborate is used as the fluxing agent) are also advantageous as an ICP-MS preparation method as acid digestion alone can be unsuitable where resistant minerals are present (e.g. rutile, zircon, chromite) or where Li and/or B addition is deemed undesirable. For example, the introduction of Li and B to ICP-MS systems (including laser ablation cells) could compromise the analytical work of other researchers (e.g. oceanographers) sharing mass spectrometry facilities who are interested in ultra-precise boron isotope measurements [9]. Flux based approaches, though effective at reducing inter-element effects, also dilute the sample thus increasing detection limits for trace elements [10,11].

Flux-less fusion techniques: Creating a glassy compact sample without a flux (flux-free or fluxless) can be advantageous in terms of speed of preparation, homogenisation, conservation of sample and long-term sample stability (for measurement and archiving). A possible disadvantage of such fluxless fusions is the volatilisation of some elements (e.g. alkali group metals, Ge, Pb and Sn [12–14]) due to the elevated temperatures required in sample preparation. An early flux-free fusion system for silicate samples was developed by Nicholls [15] who fused samples (20 mg upward) on an iridium strip in an argon atmosphere to prevent oxidation. Other later designs also used W or Mo as the metallic element or performed the fusion in Pt or Mo capsules followed by rapid quenching of the produced glass [12,15–20]. These studies demonstrated that with the correct fusion conditions, homogeneous glass beads of silicates could be produced and accurately characterised by laser ablation ICP-MS for geochemical applications. Where samples are non-siliceous (e.g. oxides and carbonates) it is necessary to add a quantity of a glass former such as silica to produce a stable glass bead for analysis.

Optimising the fusion conditions (temperature, time and composition) is critical to the homogeneity of the resulting glass bead and ensuring that all components have dissolved effectively. Geological (siliceous) samples rich in Si, Mg, Ca and Fe can be prepared at 1200 °C with fusion times of about 10 seconds whereas samples rich in Al, Si and alkali elements tend to require a longer fusion time and higher temperatures (up to 30 s and 1800 °C) [13,14] to ensure homogenisation of the more viscous Si-rich melts that are produced. The addition of pure MgO has been used by some researchers to improve the fluidity and homogenisation of Si-rich melts [14,21].

Use of pure synthetic enstatite: This study has focused on the investigation of silica-poor materials, e.g. uranium ore concentrates (UOC), oxides etc, as it is not possible to form a glassy bead unless glass-forming components are added. In this study it was considered that synthetic enstatite ($MgSiO_3$) would be an ideal silicate composition capable of dissolving complex materials that would create a glassy bead suitable for subsequent microanalysis. The enstatite was prepared by mixing high purity SiO_2 and MgO (Specpure™, Alfa Aesar) in molar proportions and the optimal ratio of sample:$MgSiO_3$ needed to produce consistent homogeneous glass bead has been investigated. The effectiveness of the overall approach was evaluated using a set of international geochemical reference samples, 2 Mn-nodule reference samples, 2 uranium ores and 4 UOCs (1 of which is certified for U and the other 3 are from a historic UK collection of UOCs)

REE in nuclear forensics: It is well established in geochemistry that graphical plots of the lanthanide group elements (or rare earth elements, REEs) can provide powerful insights into genetic processes for materials such as rocks, minerals, ores and processed ores. The plotting of normalised concentrations of La–Lu (logarithmic y-axis) against atomic number is conventionally used to visualise REE data. The normalisation involves dividing each REE concentration in a sample by its corresponding value from a chondritic meteorite which serves to remove the well-known saw-tooth abundance distribution (the Oddo-Harkins effect [22,23]). Processed uraniferous ores (UOCs) are known in many cases to retain the REE signatures of the ore or the mill from which they were derived because intra-REE variations (chemical fractionation) are expected to be limited during ore milling processes [24]. On this basis, REE patterns offer a potentially valuable characteristic that can be used in nuclear forensic investigations [24–26,] as the patterns can be directly compared to known REE patterns of U ore deposits and mills. Alternatively, the REE patterns can be used to infer geochemical associations, formation processes, mineralisation and geological type localities (i.e. geolocation).

Being able to rapidly produce and accurately analyse glass beads for REE from very small samples, particularly using highly sensitive LA-ICP-MS, is a potentially powerful investigative technique. The method has so far not been applied in the nuclear forensics field but clearly offers promise over traditional preparative methods where sample is scarce and could, for example, allow potential UOC origin to be inferred. Applications could include the analysis of illicitly recovered UOCs which contain almost no silica but which may retain a mineralogical and geochemical memory of the original ore deposit or milling facility. Additionally, this fluxless method of sample preparation and analysis could be extended to the rapid and effective analysis of other geochemical materials which inherently contain low levels of silica such as polymetallic ores and manganese nodules [27] (which can contain 30% Mn and 6% Fe but less than 5% Si).

2. Methodology

2.1 Instrumentation

2.1.1 The iridium strip fusion system

The design of the fusion device is similar to that described by Fedorowich et al. [12], but incorporates the addition of a laser pyrometer (CTM-1SF75 650-1800 °C; Micro-Epsilon ™, Germany supplied by Impress Sensors and Systems™, UK) to provide an accurate digital feedback of the temperature of the Ir-strip. The device was originally designed, constructed and tested by one of the authors (IWC; see Figure 1) and is available commercially (Raddec International Ltd, Southampton, UK). It consists of a single cylindrical aluminium chamber separated into two sections using a 1 cm thick Tufnal® insulating disc that holds two (25 mm diameter x 30 mm) copper electrodes. A 4V / 150A transformer supplies the current to the 1 mm thick Ir-strip (Heraeus, Germany) via the insulated copper terminals. Holes are drilled into the lower section of the chamber to allow good airflow around the transformer to prevent overheating. Power to the strip is supplied and controlled using a Eurotherm® thyristor circuit (Worthing, UK). Manual heat control is simply made via a ‘soft start’ potentiometer that provides a rapid and responsive control. A USB microscope with zoom allows effective observation and recording of chamber and fusion conditions. Argon is used to purge the chamber of oxygen and as argon is denser than oxygen, it is introduced at the bottom of the fusion chamber and allowed to escape at the top.

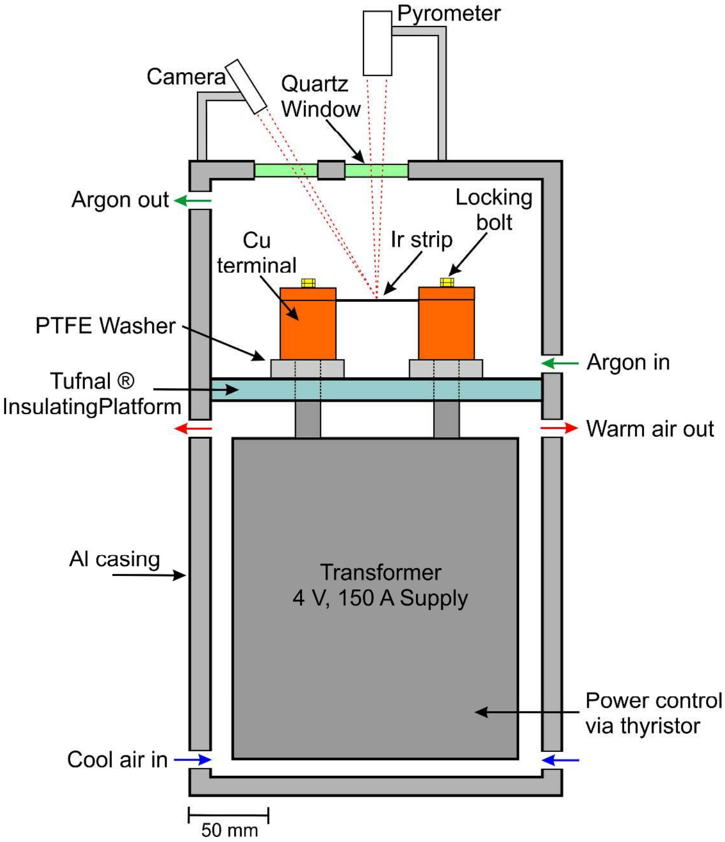

Figure 1: Schematic of the iridium-strip resistance fusion system

2.1.2 Eagle III µXRF probe

Glass bead homogeneity was initially assessed using an Eagle III™ µXRF elemental analyser (EDAX Inc®. NJ, USA) which combines an optical microscope and an XRF spectrometer fitted with a 40-300 µm Varispot polycapillary waveguide to investigate elemental composition. A Rh X-ray tube operating at 40 kV and 200 µA was used for excitation. The Eagle III™ bench top unit contains a motorised xyz stage to allow for automated elemental sample mapping of Na through to U inclusively. This µXRF unit was used to determine the appropriate blend of UOC to SiO_2 and MgO to achieve sample homogeneity prior to any laser ablation measurements due to its ease of setup and rapid analysis.

2.1.3 LA-ICP-MS

The final glass beads were ablated using an ESI® New Wave Research™ UP193FX 193 nm solid-state laser ablation system (Fremont, CA, USA) coupled to a Thermo Fisher™ X-Series II Quadrupole ICP-MS (see supporting information for operating parameters of both systems). Instrument calibration, performance and stability was performed using NIST glass standards CRMs 610 and 612 and the elemental concentrations for each CRM were taken from the GeoReM database [28–30]. The relative standard deviation for replicate element concentration measurements of the NIST CRMs were less than 5% with exception to Mg in NIST CRM 610 which was 8%. Each glass bead was measured at a minimum of 40 positions throughout the sample to investigate homogeneity and the following isotopes were measured: ^{27}Al, ^{44}Ca, ^{47}Ti, ^{55}Mn, ^{85}Rb, ^{88}Sr, ^{90}Zr, ^{93}Nb, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{232}Th, ^{238}U. Due to the significantly reduced oxide production rates caused by laser ablation and dry plasma, oxide-induced isobaric interferences were not significant.

2.2 Iridium-strip fusion

Iridium metal strips were prepared by cleaning in 40% HF followed by HNO_3 and Milli-Q® water (Millipore™, USA). Dry samples were loaded onto the centre of the Ir-strip. Powdered sample were dampened with 10 μL of Milli-Q water to form a paste to prevent the sample from vibrating off of the Ir-strip which tended to resonate when high current was passed. The fusion device was sealed and argon was allowed to flood the chamber for 2 minutes to purge oxygen from the environment to prevent oxidation of the sample. The external pyrometer was positioned so that the point from the laser is next to the gathered sample to allow for accurate temperature determination of the Ir-strip. The current was applied and adjusted to slowly increase the temperature. Once 1500 °C was reached, the sample was allowed to fuse for 1 minute at which point the current was isolated and thus quenches the melt immediately. The Ar was left to flow through the chamber to help with sample and apparatus cooling for 1 minute. The Ir-strip was carefully removed from the chamber and flexed gently to separate the glass bead.

2.3 Determining the optimal UOC to silica ratio for fusion

As previously mentioned from other studies, samples with approximately 50% SiO_2 content should produce homogeneous beads using fusion at ~1500 ℃ for > 10 s. For samples containing virtually no SiO_2, such as UOC, it is imperative that SiO_2 is added in sufficient quantity to enable the production of the glass bead but not so much that the melt becomes too viscous resulting in heterogeneity. The mass of UOC required must be kept to a minimum but should be sufficient enough that the element/isotope of interest is not below the limit of detection for the measurement technique of choice. Additionally, the final glass bead must have a sufficient surface area and depth so that multiple ablations can be made from a single sample.

High purity SiO_2 and MgO and CRM CUP-2 (CCRMP) were dried at 100 ℃ overnight to remove moisture. The SiO_2 and MgO was blended at a 1:1 molar ratio ($MgSiO_3$ or enstatite) and then milled to reduce the grain size before being blended with CUP-2 (analogous to a UOC due to its high U content – 75%) at varying ratios whilst maintaining a total sample mass of 15 mg (Table 1). This total sample mass was selected as it was found to produce good sized single glass beads without splitting into two separate and smaller glass beads. The homogeneity and degree of coalescence of the bead was assessed for varying UOC:$MgSiO_3$ ratios to determine the optimum ratio.

The six resulting glass beads were analysed via µXRF spectrometry to assess the homogeneity of the three main elements (Mg, Si and U). Each sample was secured on to the xyz stage and the sample chamber was put under vacuum. The µXRF spectrometer was operated in line scan mode for all the glass beads and additional full matrix scans were performed for the 10:90 and 20:80 glass beads.

Table 1: CUP-2:$MgSiO_3$ sample ratios & masses with total SiO_2 percentage

Ratio	Total mass (mg)	CUP-2 (mg)	SiO_2 (mg)	MgO (mg)	% SiO_2
10:90	15	1.5	6.75	6.75	45
20:80	15	3.0	6.0	6.0	40
30:70	15	4.5	5.25	5.25	35
40:60	15	6.0	4.5	4.5	30
50:50	15	7.5	3.75	3.75	25
60:40	15	9.0	3.0	3.0	20

2.4 Geochemical and uranium certified reference materials

A variety of geochemical and uranium CRMs as well as 3 UOC samples (Table 2) were prepared as glass beads using the 10:90 sample:$MgSiO_3$ blend to determine whether such a small amount of reference sample (1.5 mg) diluted with synthetic enstatite was sufficient for the accurate and precise measurement of the REEs. The geochemical CRMs were selected due to their differing REE distribution and concentration and as they represent a range of SiO_2 contents. The uranium CRMs were selected due to their range of U and SiO_2 concentrations. CRM CUP-2 is analogous to a typical UOC. The 3 UOCs were selected as their REE data have been determined via chemical separation and ICP-MS measurement external to this study [24]. A set of $MgSiO_3$ blanks were also produced to correct for element contaminants associated with the reagents.

The resulting glass beads were mounted in epoxy resin and then cut and polished to expose a smooth and flat surface. The mounted glass beads were then arranged on to a glass slide so that up to 24 separate samples including the NIST CRMs could be analysed in one session and without user intervention. Approximately 1 mm of space between the mounted glass beads and the edge of the slide was required to ensure sufficient flow of the carrier gas.

Table 2: Reference materials & UOCs investigated

Geochemical and Uranium Reference Materials

Code	Origin	Provider
AC-E	Ailsa Craig Peralkaline microgranite – UK	CRPG IWG-GIT
BE-N	Alkali Basalt – Essey-la-Cote, Nancy, France	CRPG IWG-GIT
BHVO-1	Tholeiitic Basalt – Hawaii, USA	USGS
BL-5	U-ore (7.1 wt% U) – Beaverlodge, SK, Canada	CCRMP
CUP-1	U-ore (0.1 wt% U) – Schwartzwalder, CO, USA	CCRMP
CUP-2	UOC (75.4 wt% U) – Blind River, ON, Canada	CCRMP
Mica-Fe	Biotite Mica-Fe – Massif Central, France	CRPG
NOD-A1	Ferromanganese Nodule – Atlantic Ocean	USGS
NOD-P1	Ferromanganese Nodule – Pacific Ocean	USGS
SY-2	Syenite – ON, Canada	CCRMP
SY-3	Syenite – ON, Canada	CCRMP

Uranium Ore Concentrates*

Facility	Country of origin	Deposit type
Blind River	Canada	Quartz-pebble conglomerate
Faraday	Canada	Intrusive
Rio Algom	Canada	Quartz-pebble conglomerate

* See reference 1 for further information on these UOCs.

3. Results & Discussion

3.1 Determining the optimal UOC to silica ratio for fusion

Glass beads with UOC:$MgSiO_3$ ratios ranging from 10:90 to 60:40 were prepared. For ratios greater than 30:70, the melt was viscous due to the high U content and did not coalesce into a single bead of glass, resulting in a potentially heterogeneous bead. For the two lowest ratio glass beads the melt did coalesce into a single bead but the 10:90 bead was consistently produced with good sample depth for LA-ICP-MS and homogenisation was likely to have been achieved.

The six glass beads were mounted in epoxy resin, cut and polished to expose a smooth flat surface and were measured for Mg, Si and U by the µXRF spectrometer to calculate sample homogeneity as a function of percentage standard deviation (the reproducibility of results) of the count rate. The data were collected using a line scanning mode for all glass beads and full matrix scan mode for the two lowest ratio glass beads (10:90 and 20:80). The NIST CRM 610 was also characterised to obtain a percentage standard deviation of a truly homogeneous reference material. The measured elements from the NIST 610 CRM include: Na, Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Zr and U where concentrations are all ~450 ppm.

Replicate analyses of NIST CRM 610 at different points showed a relative standard deviation of ~ 6% and therefore in this study, any value <10% from a prepared glass bead is considered homogeneous. This chosen %RSD is elevated slightly from NIST CRM 610 as this reference material has a high and uniform elemental concentration of ~450 ppm whereas elemental concentrations in the glass beads could be significantly less resulting in intrinsically elevated %RSD. The line scan results from the glass beads with UOC:$MgSiO_3$ ratio greater than 30:70 demonstrated that the glasses were heterogeneous (>15 %RSD – Table 3). The measurement points were all located towards the centre of the glass bead and avoided any anomalous topographic or surficial features. The line scan results for 10:90 and 20:80 were both <10 %RSD therefore the entire surface of each glass was measured in matrix mode, significantly increasing the number of analysis points. The matrix mode analyses demonstrated that the 10:90 and 20:80 glass beads had a percentage standard deviation of 3.26% and 8.98% respectively and are therefore considered homogeneous. The data collected from the edges of the glass were not included in the final calculation.

Table 3: Percentage standard deviations (%RSD) of the glass beads

Glass bead – UOC:$MgSiO_3$	**Line or matrix scan (analysis points)**	**%RSD of count rate***
10:90	Line (30) & Matrix (200)	3.26 (matrix)
20:80	Line (30) & Matrix (100)	8.98 (matrix)
30:70	Line (16)	14.65
40:60	Line (16)	17.98
50:50	Line (10)	24.01
60:40	Line (10)	34.25

* %RSD calculated as: 100 / Sample Standard Deviation x Sample Mean

3.2 Laser ablation ICP-MS results

3.2.1 Elemental homogeneity and volatility

The geochemical and uraniferous reference materials were prepared in duplicate as glass beads using the 10:90 sample:$MgSiO_3$ ratio and were mounted, cut and polished in resin as previously described. The glass beads were analysed using LA-ICP-MS to assess the homogeneity and elemental variation using the percentage standard deviation of major elements within the geochemical reference materials (Figure 2). The extent of homogeneity was determined from a minimum of 10 groups of 4 ablation spots randomly positioned around the surface of the polished glass bead. Anomalous results due to interaction with resin or vesicles (Figure 3), or from poor sample transmission are omitted from the calculation and are identified by the low counts of each measured element in comparison to surrounding ablation spots.

The reproducibility of the data (the percentage standard deviation of each element) is controlled by the sample homogeneity and the measurement uncertainty which is concentration dependent. The NIST 610 and 612 reference glasses are known to be homogeneous and have uniform element concentrations (~450 and 40 ppm respectively). The sample reproducibility (based on %RSD) for NIST 610 and 612 is 1.5 and 5% respectively, therefore, if a produced glass bead were to exhibit 5%

reproducibility on an element known to be at a concentration of 40 ppm or greater, the glass bead is considered to be homogeneous. For element concentrations <40 ppm, the reproducibility decreases due to measurement uncertainty and can be clearly observed with NOD-A1 and NOD-P1 where reproducibility of U is 13-15% due to the already low U concentration being diluted further by $MgSiO_3$, whereas the Mn reproducibility in the same reference standards is <4% due the exceptionally high concentration of Mn. The glass beads of geochemical reference material in this study are all deemed homogeneous based on the highest concentration elements known to be present and the reproducibility of such elements being less than or equal to 5%RSD. Elemental data that exceed 5% reproducibility typically has a concentration of <10 ppm.

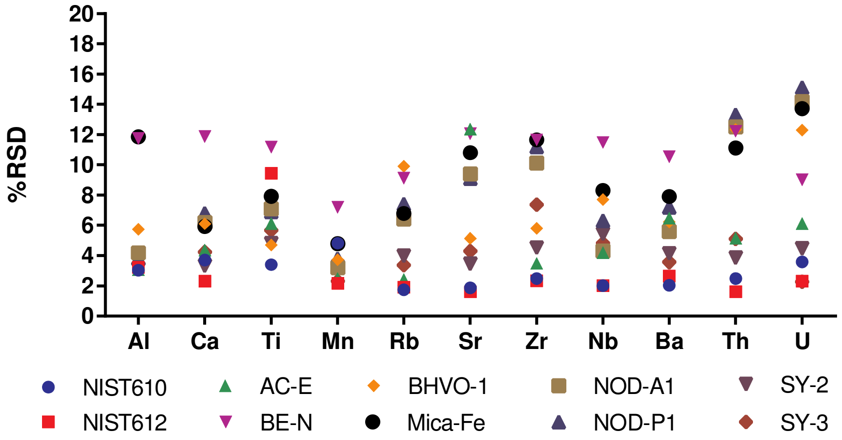

Figure 2: LA-ICP-MS %RSD values of selected elements for 10 geochemical reference materials and NIST calibration glasses. Values calculated from the mean of the duplicate glass beads

Figure 3: Resin mounted and laser ablated (circular pits) AC-E and SY-3 where resin interaction is possible due to vesicles and thin edges of glass beads.

Unlike previous studies, these geochemical reference materials have been diluted nine-fold to ensure that a glass can be produced irrespective of the original SiO_2 concentration. Therefore, the elemental concentrations are far lower than previous studies and higher percentage standard deviation values are calculated due to minor fluctuations in an already low element concentration.

Mean concentrations for Cu, Pb, Sn and Zn were between 0 and 30% of the GeoReM preferred values for SY-2 and SY-3 indicating volatilisation of these elements during fusion (Figure 4). Such volatilisation has been previously observed and relates to low condensation temperatures [13,14]. The REEs have high condensation temperatures and volatilisation is not observed in the geochemical reference materials (Figure 5).

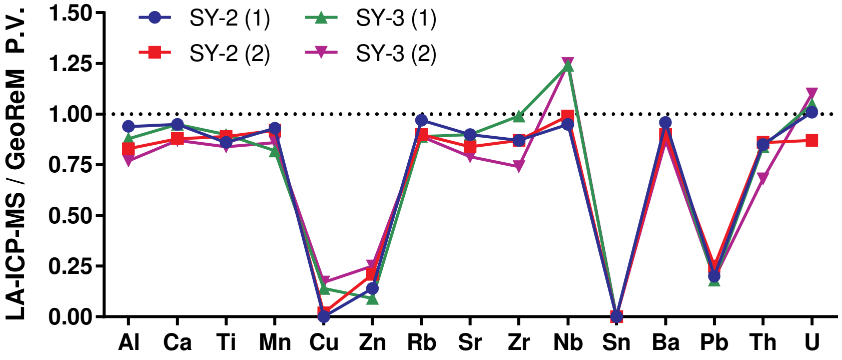

Figure 4: Ratio of measured element concentration against the GeoReM preferred or consensus values demonstrating element volatilisation of Cu, Pb, Sn and Zn.

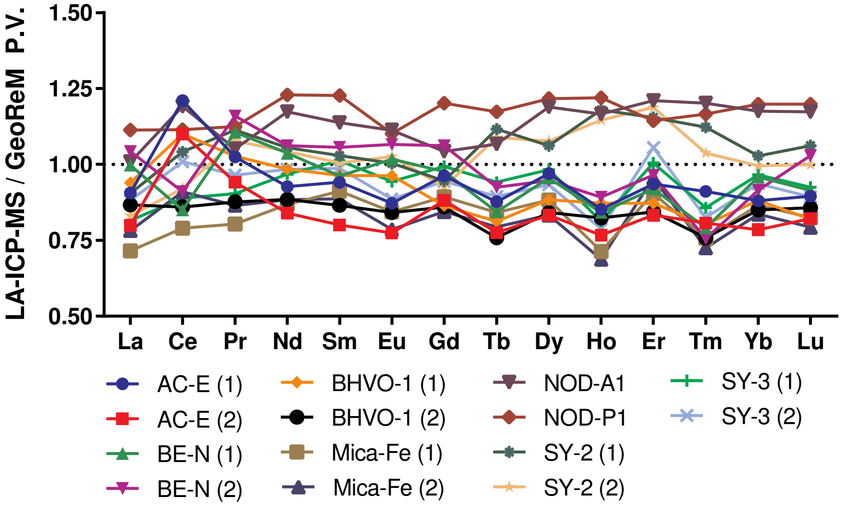

Figure 5: Ratio of measured element concentration against the GeoReM preferred or consensus values for the rare earth elements.

3.2.2 Rare earth element patterns

The REE data for each duplicated geochemical standard were plotted as chondrite normalised (REE/CI) patterns (Figure 6). Each pattern is produced from an average of at least 40 laser-ablation analysis points and have been blank and dilution corrected. Anomalous results caused by poor sample transmission or from partial interaction with a vesicle or the resin (at depth) were excluded from the calculation. Reference data are from GeoReM preferred/consensus values and the chondrite normalisation uses the data from Anders and Grevesse [31].

The REE/CI data from the glass beads have virtually identical profiles to those based on GeoReM preferred values (P.V) and demonstrate that despite the low mass of geochemical standard in the final glass bead (< 1.5 mg), accurate REE signatures can be obtained and are well above detection limits for a laser ablation setup coupled to a benchtop ICP-MS. Furthermore, the addition of $MgSiO_3$ to this wide range of geochemical reference materials has not caused any anomalous results in the patterns as a result of adjusting the SiO_2 content to approximately 50%.

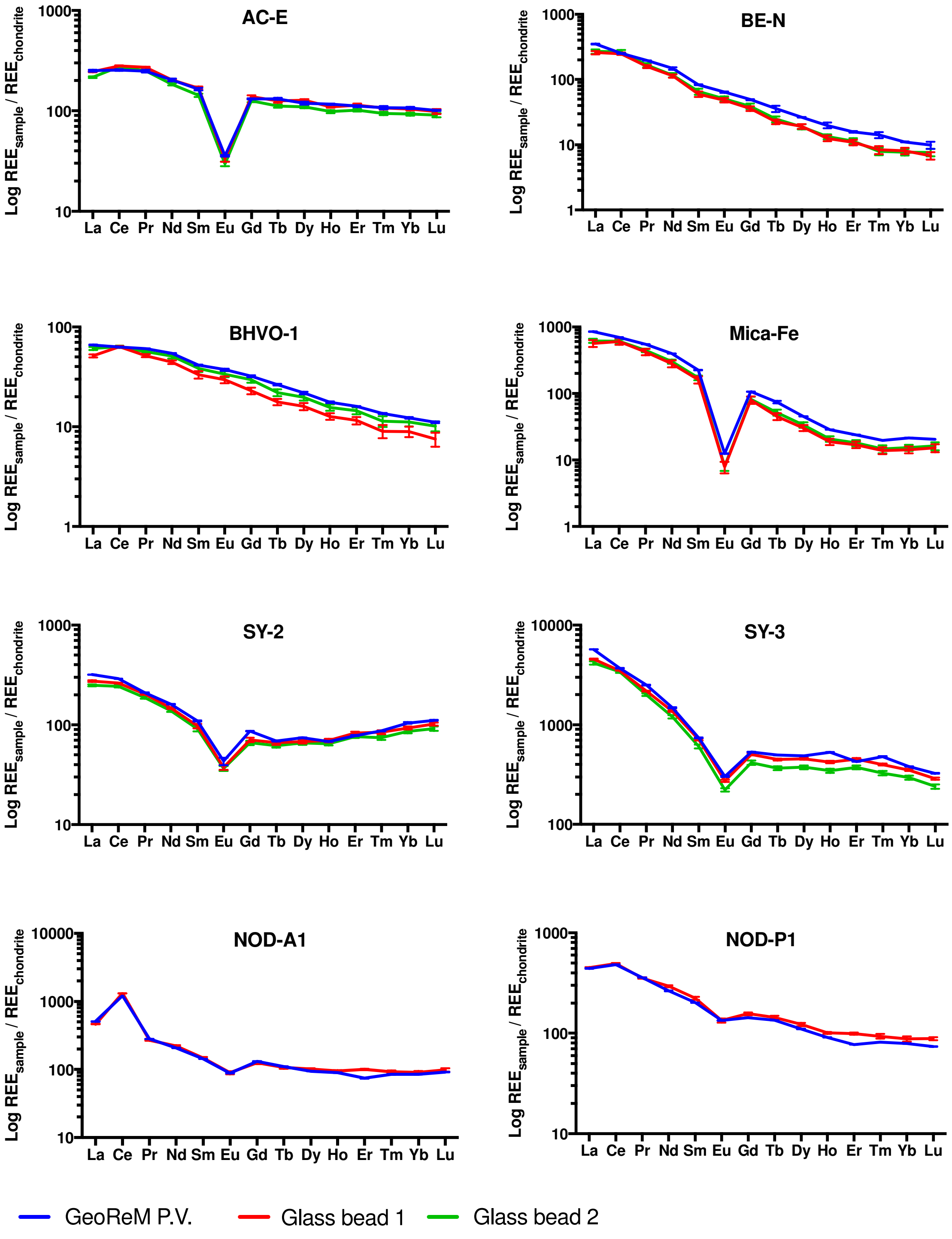

Figure 6: Chondrite normalised comparison of REE concentrations from GRM preferred values (GeoReM Database) and data from laser-ablated glass beads. Uncertainty calculated from %RSD.

Despite some elemental concentrations not perfectly matching the chondrite normalised GeoReM values, for example the relative La depletion in SY-3, the REE patterns are sufficiently close that the method provides a powerful and rapid analytical tool for applications as demanding as those found in nuclear forensics. The general profile obtained from each reference material is the indicator of a samples geological origin (for example relative Ce or Eu depletion; HREE/LREE ratio) and the overall profile comparison between the GeoReM values and the obtained LA-ICP-MS is convincingly similar.

The GeoReM values [29] are compiled from datasets using solution ICP-MS methods where chemical separation was performed to purify the analytical fraction. The samples used to produce the glass beads were not purified and yet the REE signatures are near identical to the GeoReM values despite being diluted up to 10 times and measured via LA-ICP-MS. This demonstrates that the sample preparation via fusion and analysis via LA-ICP-MS is a robust means for collecting accurate REE patterns. The similarity of the overall REE profile is more important than reproducing the individual REE concentrations, as it is the overall REE pattern, Ce enrichment, or Eu depletion that determines a samples origin.

In a nuclear forensics case, the REE signature of an illicitly recovered specimen of an unknown origin could be compared against a database of known samples in an attempt to identify a geolocation for the sample. Features such as Eu depletion (e.g. AC-E and Mica-Fe), a steady and declining REE concentration (BE-N and BHVO-1) or sharp declining light rare earth concentration relative to the heavier REEs (SY-3) could all be used to identify a possible sample match or geological setting of an unknown specimen.

Three CRMs for U (CUP-1, BL-5 and CUP-2 – Table 2) were prepared as duplicate glass beads in the same manner as the GRMs and chondrite normalised based on the average of at least 40 ablation positions and have been blank and dilution corrected (Figure 7). No reference values for REEs are available for the U CRMs but the REE patterns for 2 separate glass beads demonstrate near identical profiles and are not dissimilar to the style of pattern exhibited by the GRMs. The differing magnitude of the pattern for CUP-2 is likely due to change in sample transmission between the two glass beads or due to under or over-dilution of the original sample with $MgSiO_3$. Additionally, the sample itself may be heterogeneous and the total concentration of REE may vary throughout the reference material (CUP-2 is not certified for REE concentration) which can cause the observed difference between the two beads. Although the patterns do not perfectly correspond in concentration, they do in terms of pattern, which is the key indicator of possible geolocation or origin and is not influenced by heterogeneous REE concentration.

Three uranium ore concentrates (UOC) were prepared as glass beads as per the previous geochemical and U CRMs and chondrite normalised based on an average of at least 40 ablation positions and have been blank and dilution corrected (Figure 7). Additionally, these 3 UOCs were digested, chemically purified and concentrated using TRU™ chromatographic resin (Eichron, France) and analysed using a bench-top X-Series II ICP-MS in solution mode. These 3 UOCs have also been characterised by Varga et al (2010) [24] using a higher sensitivity instrument (Thermo Element II ICP-SFMS) and has been included for comparison. The patterns produced by the glass beads are convincingly similar to that of chemically purified fractions measured by a bench-top ICP-MS (this study) and to previously published data using ICP-SFMS.

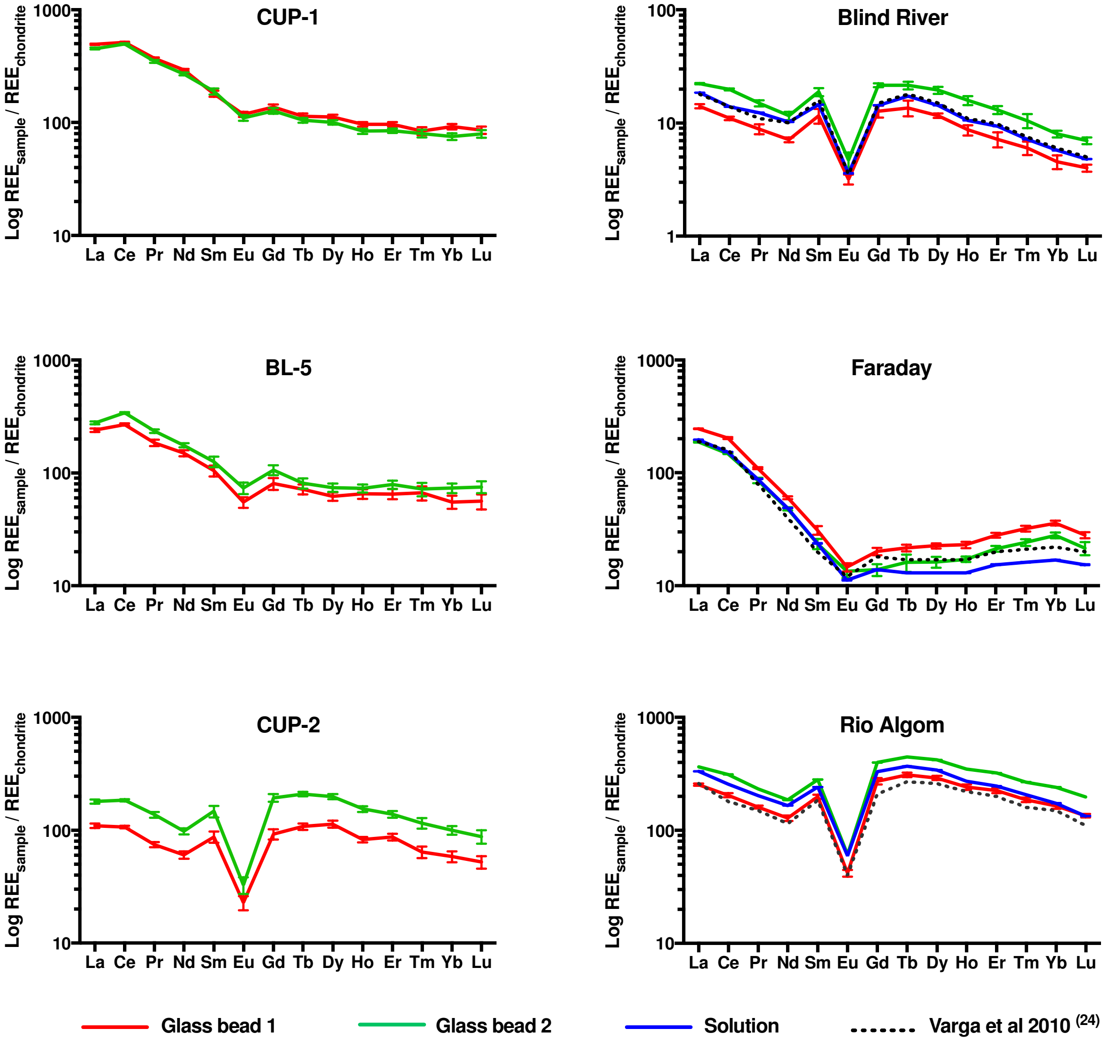

Figure 7: Chondrite normalised REE patterns for CUP-1, BL-5 and CUP-2 uranium reference materials, and Blind River, Faraday and Rio Algom UOCs obtained from 2 duplicate laser-ablated glass beads. The UOCs are compared against chemically separated and purified fractions measured via solution ICP-MS and published data (Varga et al 2010 [24]). Uncertainty calculated from %RSD.

The U CRM CUP-2 was produced at the Blind River refinery in 1986 and although the age of the Blind River UOC used in this study is unknown, the patterns between the two is again convincingly similar with a gently declining pattern from light REE to heavy REE with significant depletion in Eu – characteristic of a quartz-pebble conglomerate deposit. No matrix issues are observable in these high U-bearing samples as the signatures are of a similar nature to the geochemical reference materials. This also demonstrates that good coupling with the laser was achievable despite the high U concentration in CUP-2 and the UOCs (>70 wt% U).

The average detection limits for LA-ICP-MS of the GRMs are: La = 21, Ce = 49, Pr = 9, Nd = 52, Sm = 18, Eu = 4, Gd = 24, Tb = 2, Dy = 16, Ho = 3, Er = 4, Tm = 7, Yb = 8, Lu = 3 ppb. Although conventional solution ICP-MS methods can improve on these detection limits, it is the speed in which a sample can be prepared and analysed which is the major advantage over conventional chemical separation of the target element(s) and analysis by solution ICP-MS. A sample is typically prepared in under 10 minutes from mixing a sample with $MgSiO_3$ to producing the quenched glass bead. At this stage, the glass bead could be loaded immediately in to the sample chamber of the laser and measured. In this study, all glass beads (GRMs, uranium CRMs and UOCs - n=26) were produced in approximately 4 hours and were resin-mounted, ground and polished within 24 hours. The advantage of ablating polished level samples is that re-focussing at each ablation spot is not required and aids identification of areas of interest for analysis. Co-mounting of all samples as a single set and loading in to the sample chamber means that analysis conditions for the samples is consistent and that the laser and ICP-MS instruments are able to operate almost continuously without analyst intervention. This extended, unattended operation cannot be achieved with solution samples which can evaporate and concentrate in this time period. Due to the very little sample handling, few additional compounds (MgO and SiO_2) used and no requirement for chemical purification or extended exposure to possible contaminants in the laboratory, the associated procedural blank for producing glass beads is comparatively low. The small sample handling also reduces radiological risk, minimises cross contamination and (importantly for nuclear forensics) preserves more of the suspect material for further analyses.

4. Conclusions

Nuclear forensic studies of difficult to dissolve materials (in mineral acids) such as uranium ore concentrates (UOCs) or uraniferous ores can be challenging and can benefit from novel technologies. This study has developed a fusion technique that conserves material, is rapid and which produces a robust and homogenous glassy sample for subsequent LA-ICP-MS analysis. A novelty of the method is the use of high purity MgO and SiO2, in enstatitic stoichiometry, $MgSiO_3$, to fuse a range of silicates, low silica and oxide-rich samples (GRMs, UOCs, ferromanganese nodules) into glassy beads without a fluxing agent. All samples, after mixing with synthetic enstatite (sample:flux of 1:9), formed homogeneous glass beads when heated on an iridium strip heater at 1500℃ for 1 minute. Samples as small as 1.5 mg could be effectively dissolved in the enstatite melt and after a few seconds cooling the quenched glass bead could be readily removed from the Ir strip for subsequent analysis. The method was tested for such small samples to show what might be achievable when testing scarce seized materials

Glass beads, prepared from 8 geochemical reference materials, (GRMs), 3 certified uranium reference materials (CRMs) and 3 uranium ore concentrates (UOC) were mounted and ground flat ready for LA-ICP-MS analysis. The resulting normalised REE patterns for the geochemical reference materials are impressively similar to normalised GeoReM [29] consensus values obtained from chemically separated fractions and measured by conventional solution ICP-MS methods. Additionally, the U CRMs demonstrate that their patterns can be reproduced despite elemental heterogeneities and UOC patterns are near identical in comparison to chemically purified and concentrated samples analysed via solution ICP-MS methods. A further improvement in sample reproducibility from fluctuation in sample transmission could be made by intimately mixing an enhanced quantity of the REE thulium [32] into the enstatite mixture.

The developed method shows that reliable REE profiles can be obtained from even very small homogenised glass samples. The sample preparation and fusion time is typically <10 minutes and many (up to 20 in this study) glass beads can be loaded in the sample chamber of the LA-ICP-MS system allowing for unattended, efficient data acquisition. In future, this data could be compared against a database of known samples in order to help identify a geological setting, particular deposit or uranium mill in which a sample may have originated in order to benefit nuclear forensic investigations.

5. Acknowledgements

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Supporting Information. Table S-1: LA-ICP-MS instrument parameters

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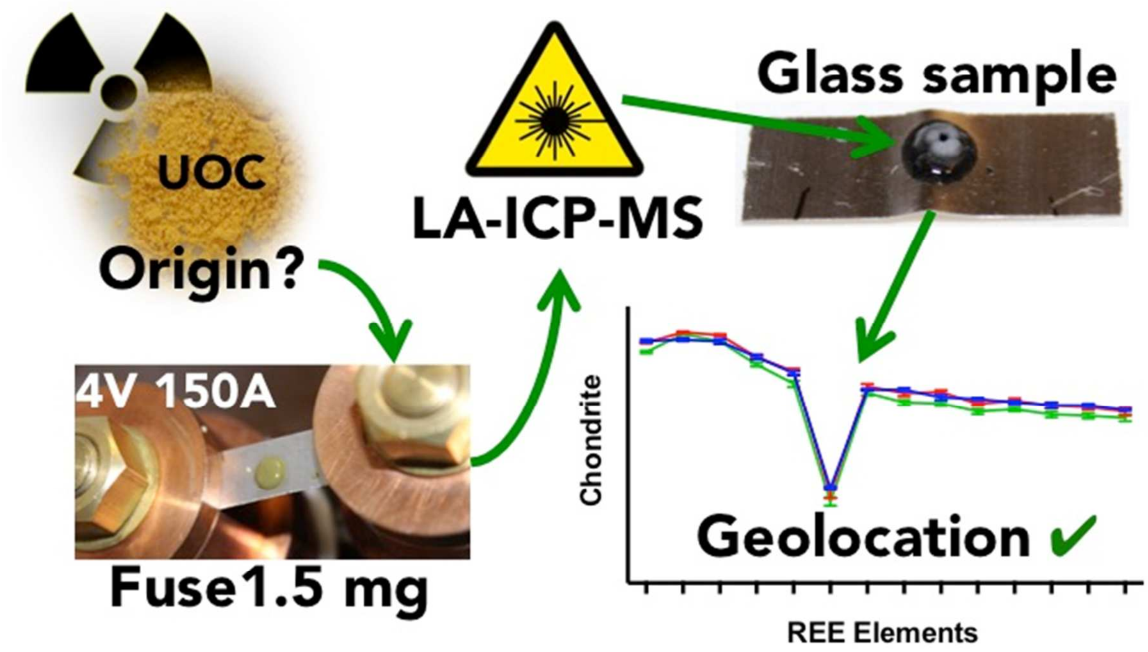
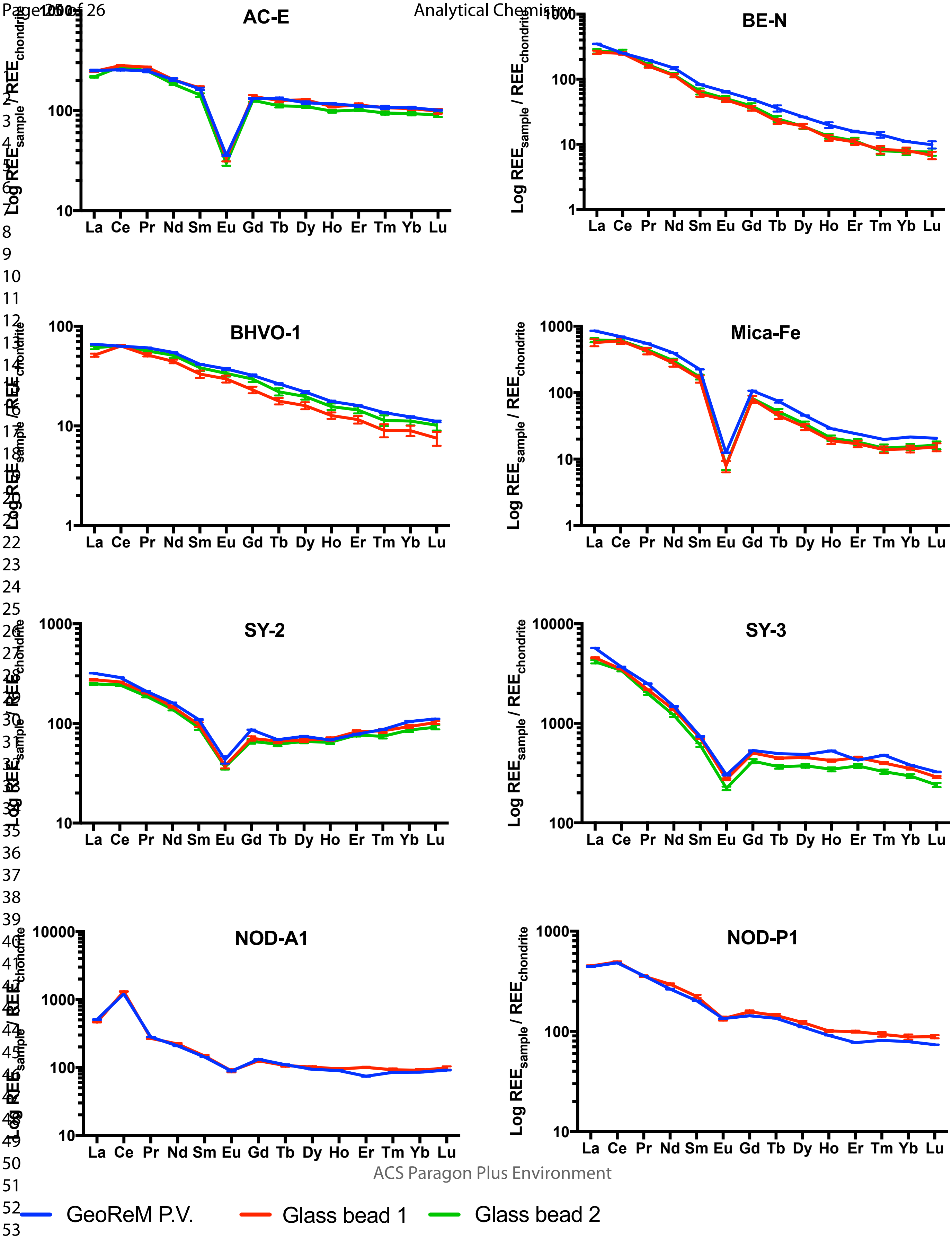
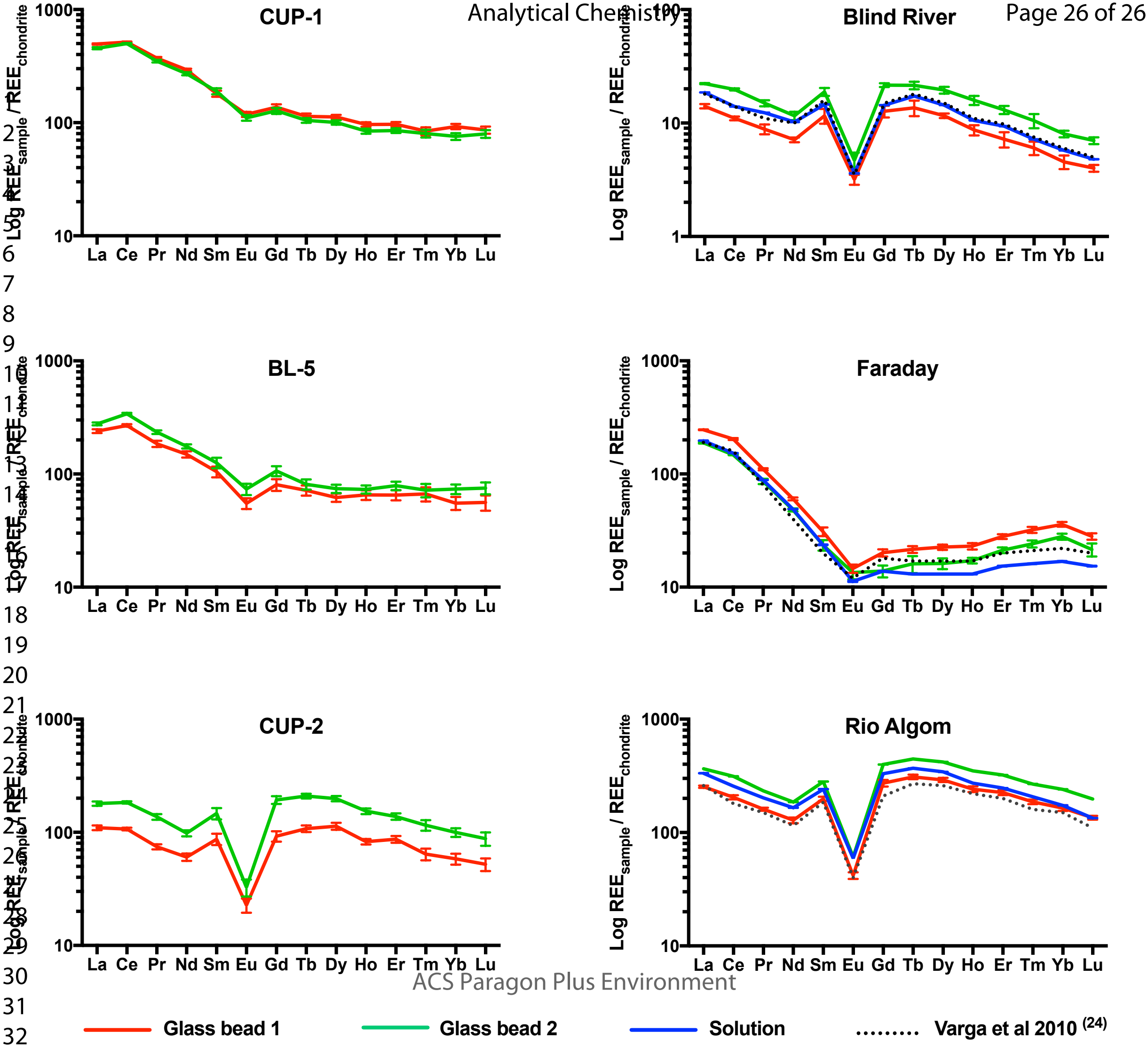
TOC ONLY


UOC
Origin?
LA-ICP-MS
Glass sample
4V 150A
Fuse1.5 mg
Chondrite
Geolocation ✓
REE Elements


AC-E
BE-N
BHVO-1
Mica-Fe
SY-2
SY-3
NOD-A1
NOD-P1
Log REE_{sample} / $REE_{chondrite}$
10
100
1000
10000
1
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
GeoReM P.V.
Glass bead 1
Glass bead 2


CUP-1
Blind River
BL-5
Faraday
CUP-2
Rio Algom
Log REE$_{sample}$ / REE$_{chondrite}$
1000
100
10
1
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Glass bead 1
Glass bead 2
Solution
Varga et al 2010 (24)