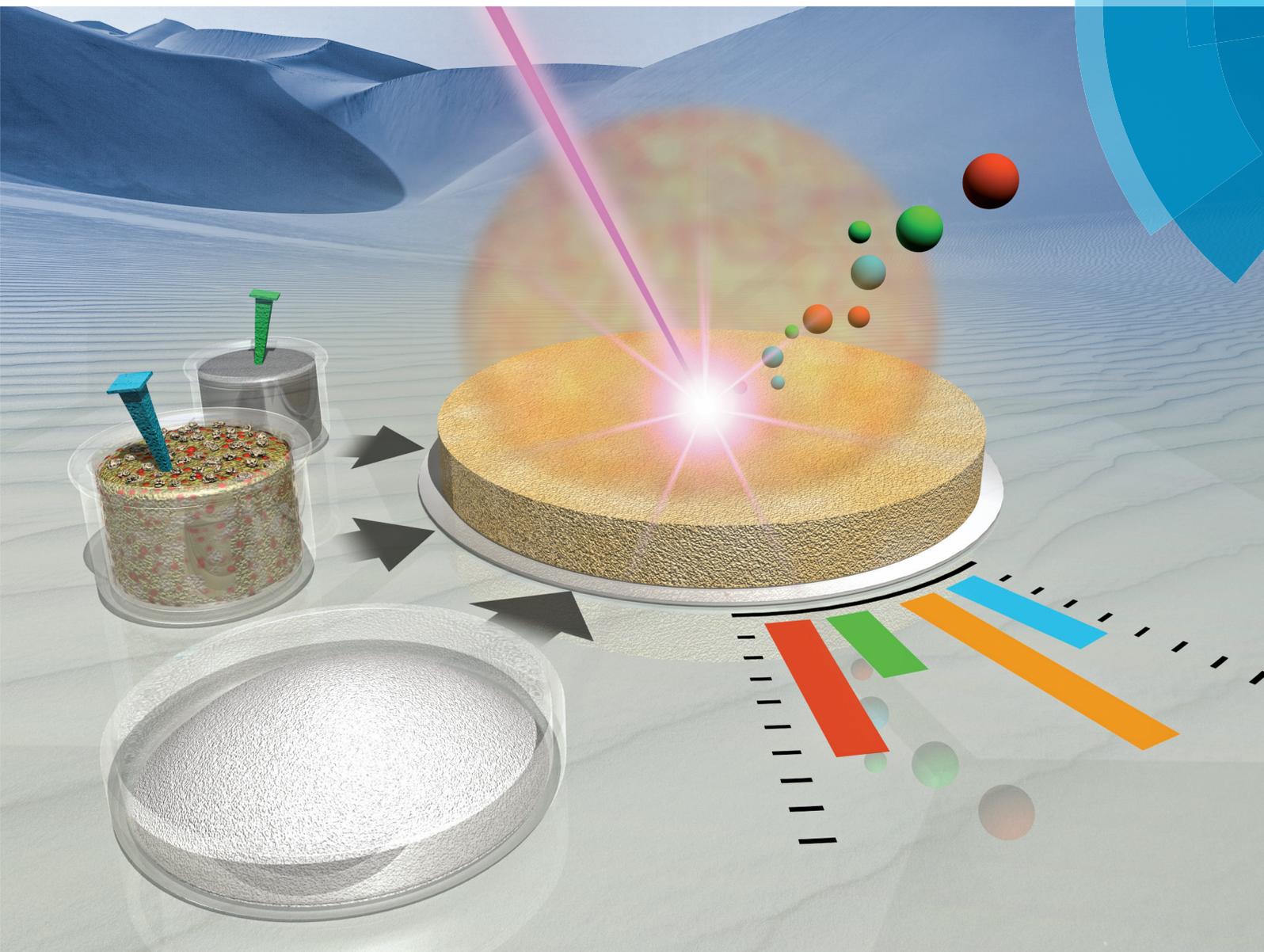


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Solid matrix transformation and tracer addition using molten ammonium bifluoride salt as a sample preparation method for laser ablation inductively coupled plasma mass spectrometry

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Solid sampling and analysis methods, such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), are challenged by matrix effects and calibration difficulties. Matrix-matched standards for external calibration are seldom available and it is difficult to distribute spikes evenly into a solid matrix as internal standards. While isotopic ratios of the same element can be measured to high precision, matrix-dependent effects in the sampling and analysis process frustrate accurate quantification and elemental ratio determinations. Here we introduce a potentially general solid matrix transformation approach entailing chemical reactions in molten ammonium bifluoride (ABF) salt that enables the introduction of spikes as tracers or internal standards. Proof of principle experiments show that the decomposition of uranium ore in sealed PFA fluoropolymer vials at 230 °C yields, after cooling, new solids suitable for direct solid sampling by LA. When spikes are included in the molten salt reaction, subsequent LA-ICP-MS sampling at several spots indicate that the spikes are evenly distributed, and that U-235 tracer dramatically improves reproducibility in U-238 analysis. Precisions improved from 17% relative standard deviation for U-238 signals to 0.1% for the ratio of sample U-238 to spiked U-235, a factor of over two orders of magnitude. These results introduce the concept of solid matrix transformation (SMT) using ABF, and provide proof of principle for a new method of incorporating internal standards into a solid for LA-ICP-MS. This new approach, SMT-LA-ICP-MS, provides opportunities to improve calibration and quantification in solids based analysis. Looking forward, tracer addition to transformed solids opens up LA-based methods to analytical methodologies such as standard addition, isotope dilution, preparation of matrix-matched solid standards, external calibration, and monitoring instrument drift against external calibration standards.

Introduction

Laser ablation (LA) is a means of direct solid sample introduction to inductively coupled plasma (ICP) mass spectrometry (MS); it avoids acid dissolution and chemical separation steps that are conventionally associated with solid sample analysis. Indeed, phrases like minimal, little, or no sample preparation are often used in expressing the benefits of sample analysis by LA-ICP-MS,^{1–4} although strictly speaking these comments refer to no wet chemical sample preparation. Sample preparation methods such as milling, pulverizing, and pressing to a powder, with or without binders or other additives, are common. Nevertheless, sample digestion and wet chemical sample preparation are generally separate endeavors from LA-ICP-MS. At the same time, certain issues with LA-ICP-MS are often mentioned in critical reviews,^{1,2,4–9} including solid matrix variability and its influence on the ablation processes, matrix dependent elemental fractionation, lack of matrix-matched standards for external calibration, and limitations to internal calibration because it is challenging to add and distribute spikes into solid samples. These are issues that wet chemical sample preparation overcomes by digesting a solid sample and diluting it into a liquid matrix before analysis. In this paper we introduce the concept of a synergistic minimal sample preparation method that is used in combination with LA-ICP-MS as a means to overcome such issues. The aim of this minimal sample preparation procedure is to reactively transform the original matrix, breaking down solid oxides, silicates and aluminosilicates of the original matrix, while enabling the addition of spikes for improved internal calibration in the absence of matrix-matched external standards. In conjunction with ICP-MS, we call this SMT-LA-ICP-MS, where SMT is derived from solid matrix transformation including the option to add spikes as tracers. This concept is shown schematically in Fig. 1.

In most traditional sample preparation methods, the original matrix is broken down and dissolved. The most common

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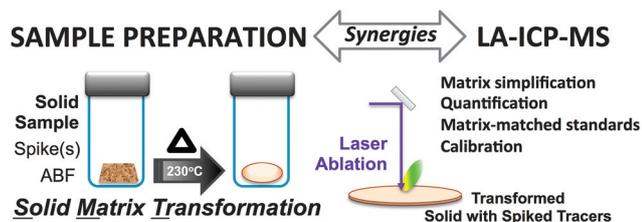


Fig. 1 Concept for synergism between sample preparation and LA-ICP-MS, entailing a minimal sample preparation approach that transforms potentially heterogeneous samples of diverse matrixes to a more consistent matrix with the option for spike addition, thus facilitating improved quantification by methods such as isotope dilution, the creation of matrix-matched standards, and solid materials for instrument calibration.

approaches include dissolution in boiling acids at atmospheric pressure, microwave assisted acid digestion in high-pressure apparatus, or alkali fusion followed by aqueous dissolution.^{10–12} Often multiple steps in sequence are required. It has been noted that even conventional methods, especially those with liquid acids, do not always fully solubilize and recover uranium (or other refractory elements) from a solid sample.^{10–12} Recently, the use of molten ammonium bifluoride (ABF) was introduced as a means of breaking down sample matrixes before chemical analysis.¹³ Molten ammonium bifluoride at 230 °C can break down mineral samples rapidly, without open boiling acids, high-pressure apparatus, or the addition of large masses of solid alkali. The initial matrix decomposition process entails simply placing milligram quantities of the solid mineral sample in a PFA fluoropolymer vial with an appropriate ratio of solid ABF, sealing the vial with a screw-top lid, and placing it in the oven. After reaction at a moderate temperature, cooling yields a new solid material.

In a wet chemical sample analysis approach, Zhang *et al.* processed felsic mineral samples, using a sequence of ABF reaction at 230 °C in sealed PFA vials, followed by further closed vessel treatment with liquid nitric acid, evaporation, dissolution in an acid solution, addition of internal standard(s), and dilution for liquid-nebulization ICP-MS analysis.¹³ Hubley *et al.* followed a very similar procedure for the decomposition and dissolution of milled trinitite glass for liquid nebulization ICP-MS.¹⁴ In our laboratory, we have confirmed that diverse materials such as glass, milled quartz, standard reference sediments, and uranium ore standards can be fully decomposed by similar methods; zircon is challenging.¹⁵ When used for sample dissolution, additional steps using nitric acid follow the ABF method. However, the initial step with ABF that transforms the original sample to another solid sample is relatively simple and rapid.

Here, our interest is to investigate how solid samples derived from ABF decomposition might be used with direct LA solid analysis rather than serving as a step toward dissolution (Fig. 1). The ABF decomposition takes diverse and potentially heterogeneous solid samples and transforms them reactively

in molten ABF to solid materials consisting of the reaction products (such as metal fluorides, which had been mostly metal oxides in the original solids) and remaining ions from the ABF reagent. This procedure provides the opportunity to add one or more isotopic or elemental spikes to the sample which then become dispersed in the transformed solids. Spike addition to transformed solids opens up LA-based methods to analytical methodologies such as standard addition, isotope dilution, preparation of matrix-matched solid standards, external calibration, and monitoring instrument drift against calibration standards.

In this communication, we provide proof of principle experiments with uranium ore showing that these simple procedures in PFA vials yield transformed solids that can be directly sampled, without further dissolution or dilution, by LA, and that the solids can be prepared to contain elemental and isotopic spikes.

Experimental

Reagents, samples, and standards

Low grade uranium ore (pitchblende) standard reference material S-12, for use as a sample, was obtained from the IAEA's Analytical Quality Control Service (AQCS).¹⁶ This standard has a certified value of 0.014 wt% U₃O₈, which calculates to 120 µg g⁻¹ U. Ammonium bifluoride (ABF) salt was acquired from Sigma-Aldrich (St Louis, MO) Trace Metal (99.999%) grade, and used as received. Optima™ grade nitric acid was purchased from Fisher Scientific (Waltham, MA). Solutions were prepared from deionized water (18.3 MΩ cm) using a Barnstead Nanopure Diamond water purification system (Dubuque, IA).

Single element NIST-traceable standards (1000 ppm) for Bi, Tb, and In were obtained from High Purity Standards (Charleston, SC). The In standard was 95.7% In-115 and 4.3% In-113, whereas the Bi and Tb, were 100% Bi-209, and Tb-159, respectively. A gravimetrically determined mass of 99.93% enriched uranium (*i.e.*, 99.93% U-235) metal, obtained from an in-house supply, was dissolved in acid and brought to a known volume. Its concentration was verified using an Agilent 7700X ICP-MS (Ventura, CA).

Matrix transformation procedures

Decomposition of inorganic media by molten ABF was performed in sealed PFA reaction vessels (7 mL flat-bottom PFA vials (Saville)) using a UF55 programmable convection oven (Mettler GmbH, Schwabach, Germany). In the general procedure, low grade uranium ore standards were processed in PFA vials by mixing *ca.* 50 mg of the standard, serving as the sample, with up to 300 mg ABF, sealing the vial and heating to 230 °C for at least one hour. After cooling, the molten salt solidified into a somewhat soft solid mass in the bottom of the vial. Solids were pressed to make flat samples for LA-based measurements with ICP-MS or LIBS. Sample pressing was performed to create a flat surface, using a manual Parr Pellet

Press model 2811 with a diameter of 0.5 inch (1.27 cm) pressing for 5 seconds.

For addition of spikes, single element standards of In, Tb, and Bi, and the isotope U-235 were added at $6 \pm 0.3 \mu\text{g}$ each element, and dried into the sample powder. The sample was 50.49 mg of uranium ore standard S-12, calculated to have 5.994 μg natural U based on certificate value of 140 $\mu\text{g g}^{-1}$ U_3O_8 , and hence 5.95 μg U-238 with 0.043 μg U-235, based on natural U isotopic abundances.¹⁷ The precise amount of U-235 spike contained $6.04 \pm 0.01 \mu\text{g}$ U-235, which is $2.57 \times 10^{-8} \pm 4.2 \times 10^{-10}$ moles. At 99.93% isotopic purity, this spike contained a largely negligible amount of U-238: 1.80×10^{-11} moles. The ABF mass in this reaction was 300.22 mg, giving an ABF : sample = 6 : 1. The reaction in molten ABF at 230 °C was carried out in the sealed PFA vial for 6 hours, and cooled to yield a Stage 1 solid mass with spike addition for LA-ICP-MS investigations.

In some experiments, uranium ore standards were broken down by the ABF method, yielding Stage 1 solids, followed by dissolution and heating in nitric acid, and then evaporation, yielding Stage 2 solids. This process entailed the addition of 2 mL concentrated nitric acid, and heating in the sealed vial at 160 °C in a hot block for 1 hour, followed by open vessel evaporation to dryness at 160 °C leaving another soft solid mass (Stage 2). For wet chemical analysis of the U-238 recovery, Stage 2 samples were dissolved in 1 mL concentrated nitric acid plus 2 mL water, capped, and heated to 120 °C for 6 hours, to yield fully dissolved sample in solution for analysis by liquid nebulization ICP-MS (Agilent 7700X, Ventura, CA).

Instrumentation and laser-based analysis procedures

The experimental system consisted of a laser ablation system (J200 Tandem, Applied Spectra, Inc.) coupled to a ICP time-of-flight (TOF) mass spectrometer (ICP-TOFMS Optimass 9000) from GBC scientific. The laser was a frequency quintupled Nd:YAG nanosecond (ns) laser at 213 nm and was focused onto the sample surface by a UV microscope objective lens. Laser ablated aerosol was transported from the ablation chamber to the ICP-TOF-MS with helium as a carrier gas, while argon was added to the gas stream as a makeup gas. The plasma optical emission (LIBS) from the laser-sampling location was imaged onto an optical fiber bundle with a UV fused-silica plano-convex lens; the other end of the fiber was directly connected to the entrance slits of a six channel spectrometer, each equipped with a CCD array detector (Aurora from Applied Spectra). The gate of the CCD array was triggered by the ns-laser. The experimental conditions are listed in detail in Table 1. The J200 Tandem system has two cameras, a "Macro-camera" to image the ablation chamber, and a "Micro-camera" take pictures of the ablation site through the objective lens.

Nine locations on the sample were analyzed with LA-ICP-MS consecutively (each location representing a replicate of the sample under study). A delay between each location of 15 seconds was used to avoid any mixing of the ablated aerosol before leaving the ablation chamber. Fifty laser shots

Table 1 Instrumental parameters

Laser ablation/translation stage system	J200 Tandem
Wavelength	213 nm
Pulse length	5 ns
Repetition rate	10 Hz
Energy per pulse	6 mJ
Spot size	80 μm
Number of laser pulses	50
Number of locations	9
Mass spectrometry	
ICP-TOFMS system	GBC scientific
RF power	1200 W
Plasma Ar flow rate	12.0 L min^{-1}
Auxiliary Ar flow rate	0.60 L min^{-1}
Carrier(He)/make-up (Ar) flow rate	0.70/0.70 L min^{-1}
Acquisition time	1 s
Acquisition rate	29.41 kHz
Total spectra per reading	29.41 K
Optical spectrometry	Aurora
Optical spectrometer system	Czerny turner
Detection channels	6
Detector	CCD
Gate width	1.05 ms
Gate delay	0.2 μs

were used for each location at a repetition rate of 10 Hz, which resulted in a total ablation time of 3 minutes.

Results and discussion

Matrix transformation approach

Ammonium bifluoride (ABF), with chemical formula of $\text{NH}_4\text{F}\cdot\text{HF}$ or $\text{NH}_4\cdot\text{HF}_2$, is a solid with melting point ~ 125 °C and a boiling point ~ 240 °C. It can be purified by sublimation to separate it from trace metal impurities. In molten salt reactions at 230 °C, the temperature is higher than boiling acids in open containers (*e.g.*, boiling points of concentrated nitric, hydrochloric, and hydrofluoric acids are each below 125 °C), which is advantageous for breaking down resistant minerals, yet still below the boiling point of ABF; hence processes can be carried out without requiring high-pressure vessels.¹³ In addition, given the simple approach, large numbers of samples can be processed in parallel. Pitchblende uranium ore samples were decomposed by reaction with molten ABF at 230 °C in sealed PFA vials as described in the Experimental section. The solids formed after cooling, denoted Stage 1, were pressed into flats for laser ablation experiments.

In preliminary experiments on uranium ore sample materials, the extent of sample matrix decomposition initiated by reaction with ABF was assessed by dissolving Stage 1 solids in nitric acid as described in the Experimental section, and filtering to determine the recoverable undissolved solids. ABF : sample ratios up to 6 : 1 were investigated with reaction times up to 6 hours. As long as the ABF : sample mass ratio was greater than or equal to 4, and the reaction time at 230 °C was at least one hour, the fraction of the original sample mass

that dissolved was 99.8% or higher. At a 6 : 1 ratio at one hour (the shortest time tested) the dissolved fraction was 100%.¹⁵ Similarly, at a 4 : 1 ratio with reaction times of 2, 4, or 6 hours, the dissolved fraction was 100%.

Further experiments were performed to assure that U from the original sample was not lost in these sample handling procedures. Samples of S-12 standard were processed through reaction with ABF, yielding the Stage 1 solids. They were dissolved in nitric acid, heated, and evaporated again, yielding a new solid matrix that we call Stage 2 (see Experimental section). The stage 2 solid was dissolved, diluted and analyzed using liquid nebulization ICP-MS. The certified concentration of U in the ACQS low grade uranium ore S-12 was $120 \mu\text{g g}^{-1}$ (to one sigma). The chemical recovery of U-238 from the 50 mg scale decomposition and dissolution process starting with ABF was $107\% \pm 8\%$ in assessment of 8 replicates. For comparison, three one-gram samples of S-12 were digested by a microwave digestion procedure, and the recovery was $98\% \pm 10\%$.¹⁵ Both analyses were consistent with the certified value. Regarding ABF matrix transformation in a sealed PFA vial, we conclude that neither the ABF matrix transformation procedure, nor subsequent processing with nitric acid including open vessel evaporation, leads to any measurable losses in the sample uranium content.

SMT-LA-ICP-MS on certified uranium ore with tracer

Solid samples from the reactions with ABF in PFA vials (*i.e.*, Stage 1) were soft materials that can be easily pressed into flat discs for subsequent laser ablation. This action also pressed out voids present in some samples and provided flat surfaces for maintaining laser focus when moving from spot to spot. These pressed solids were readily ablated with the nanosecond laser used in these studies. Representative pressed Stage 1 samples before and after laser ablation, are shown in Fig. 2. The second image shows the 3×3 array of ablation spots.

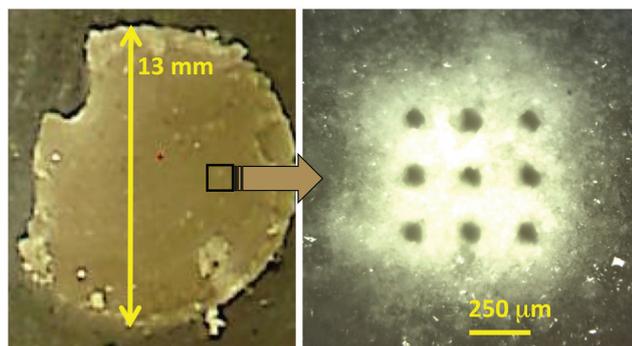


Fig. 2 Photographic images of the pressed Stage 1 solid derived from reaction with molten ABF, and a 3 by 3 pattern of ablated spots in the pressed Stage 1 solid. The disc in the first image has a diameter of ca. 13 mm from the press; the region where ablation spots will be taken is indicated in the black square rectangle. The 3×3 array (second image) is 0.5 mm on a side. The laser spot size was $80 \mu\text{m}$. Bright contrast in the second image is due to debris from laser ablation. The two images were taken with different cameras (see Experimental section).

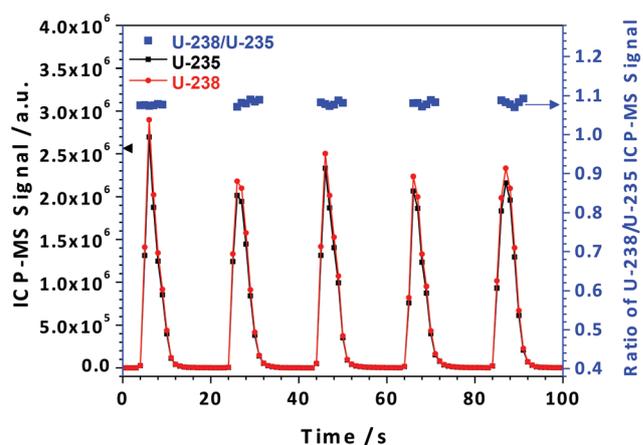


Fig. 3 Temporal signals for U-238, U-235, and the U-238/U-235 ratio for five ablation spots from the Stage 1 solid derived from reaction of the uranium ore S-12 sample with molten ABF where spikes had been added prior to heating the reaction (a.u. = arbitrary units).

Fig. 3 shows the temporal LA-ICP-MS signals for U-235, U-238 and the U-238/U-235 ratio from five spots of the uranium ore S-12 sample containing tracers. Integrated data from all nine ablated spots of the 3×3 array are provided in Tables 2–4. For these specific measurement conditions and samples, the relative standard deviation between the nine locations for all studied isotopes (Table 2) were around 19%. For the U-238 and U-235 signals, the relative standard deviations were 17% (Table 2). Previously reported LA-ICP-MS results¹⁸ on NIST glasses 610 and 612 were consistent with those found in the present study; specifically, the %RSDs for the NIST 610/612 glasses were around 12%. The slightly lower precision for the present work is attributed to spikes in the transient signals produced by large particles ablated from the Stage 1 solid.

Table 2 SMT-LA-ICP-MS average signals for U-238 and the tracer isotopes

Isotope	Average	%RSD
In-115	1 380 000	19
Tb-159	2 230 000	22
Bi-209	3 830 000	19
U-235	7 897 195	17
U-238	8 513 979	17

Table 3 Reproducibility between spot locations taking the ratio of U-238 to tracer isotope

Isotope ratio	Average	%RSD
U-238/U-235	1.0795	0.1
U-238/In-115	6.2	8.8
U-238/Tb-159	3.8	8.7
U-238/Bi-209	2.2	12

Table 4 Repeatability measurement for the U-238/U-235 ratio at each ablation spot

Avg. 238/235	Std. dev.	%TRSD
1.0761	0.0017	0.16
1.0829	0.0070	0.64
1.0803	0.0051	0.47
1.0807	0.0056	0.52
1.0827	0.0079	0.73
1.0786	0.0081	0.75
1.0792	0.0046	0.42
1.0790	0.0048	0.44
1.0810	0.0039	0.36

Because the ABF-based matrix transformation enables the addition of spikes, our goal in these experiments was to investigate spike addition to the solid sample and its influence over U-238 signal precision. Two of the metrics we used to describe precision were repeatability and reproducibility after taking the ratio the U-238 signal to those of the added tracers (ratios reported in the tables are simply intensity ratios of the signals without correction for detector response.) The reproducibility describes the variation among the nine locations and is measured by the relative standard deviation (%RSD), while the repeatability is defined as the fluctuation within individual locations and is measured by the temporal relative standard deviation (%TRSD), as defined previously.^{19,20}

Table 3 shows the average reproducibility results across the ablation spots for the U-238 ratio to each of the tracers. It is evident, as was expected, that in every case the tracers improved the reproducibility between locations. Exceptional improvement was obtained when U-235 was used as a tracer, where the U-238 %RSD improved from 17% to 0.1% after division by U-235 signal—an improvement of over 2 orders of magnitude.

The repeatability of the transient signal within each spot, *i.e.*, the %TRSD, is given in Table 4. Within each location, the U-238/U-235 ratio varied with values ranging from 0.16 to 0.75%. The consistency of the U-238/U-235 ratio within spots (using %TRSD) and across the nine spots (using %RSD, 0.1%) indicates that the U-235 spike was evenly distributed in the sample. Although the laser ablation solid sampling process is subject to variability in the mass ablated, the particles ejected or condensed, particle transport, and digestion in the ICP, the isotopic ratios for isotopes of the same element, enabled by adding the spike, are dramatically more consistent in these experiments.

With regard to the other tracers (In, Tb and Bi), only a modest improvement in the U-238 consistency was obtained compared to the U-235. Our previous study¹⁸ from NIST 610/612 glasses showed that, when the U-238 signal is ratioed to that of Th-232, the precisions improved slightly to about 9%. Our results are consistent, being close to 9% for In and Tb, and 12% for Bi. Elemental fractionation can occur due to vaporization and particle formation from the plasma, and varying digestion of different particle sizes in the ICP. With nanosecond laser ablation, fractionation effects have been noted in the literature and attributed to factors like the particles sizes and particle vaporization effects.^{21,22}

The average ratio values for U-238/U-235 in Tables 3 and 4 are the results of the direct ratio of the raw signal without correction for detector response. Although the process has not been optimized, some straightforward calculations are illustrative. Without accounting for plasma fractionation behaviors or detector calibration, using the ratio of the raw signals for U-238 to U-235 (*i.e.*, 1.08), one can multiply the moles of U-235 from the spike to get an approximation for the moles of U-238 in the sample and hence a mass concentration of 131 $\mu\text{g g}^{-1}$ U-238. Performing a full isotope dilution calculation, taking into account the slight amount of U-238 in the U-235 spike and the natural U-235 in the ore sample, one obtains an estimate of 132 $\mu\text{g g}^{-1}$ U-238. These values compare with the certificate value of 140 $\mu\text{g g}^{-1}$ U₃O₈, (two significant figures and no uncertainty reported), and corresponding to 118 $\mu\text{g g}^{-1}$ U-238, and to our own solution based ICP-MS analysis of S-12 samples at $128 \pm 9 \mu\text{g g}^{-1}$ U-238. Without corrections, it is expected that the LA-ICP-MS results will bias to higher U-238 values relative to the lighter spike U-235.

There is no indication from these matrix transformation experiments that this method fails to fully measure sample uranium content. The results here indicate that the ABF-based solid matrix transformation method provides a new mass spectrometric analysis approach without the need for complete wet chemical digestion and dissolution (or time-consuming chemical separations), and the attendant possibilities for incomplete dissolution and recovery. The latter may be a concern in a liquid nebulization approach if a solid dissolution method failed to fully solubilize and recover uranium or other elements of interest.^{10,11}

Matrix investigation using LIBS

We briefly investigated the transformed matrix using laser induced breakdown spectroscopy (LIBS) for lighter elements that are often difficult to measure in ICP-MS. Selected low (a) and high wavelength (b) spectral regions are shown in Fig. 4.

The atomic emissions in these spectra show that the Stage 1 solid after transformation with ABF contains sample-derived Si and ABF-reagent-contributed F. We also examined solids derived from nitric acid dissolution of the Stage 1 ABF solid, with closed heating and open evaporation, yielding another transformed matrix we call Stage 2. In this new solid, atomic emission from silicon and the fluorine were no longer observed. The loss of Si is readily explained by the fluorination of Si in the sample to SiF₄ during the ABF reaction, and loss as a volatile gas during the nitric acid process leading to Stage 2. In addition, the reagent-contributed F has been driven off as well. This represents further transformation of the matrix at Stage 1 from a fluoride rich matrix to a more nitrate-based matrix at Stage 2, while also removing some of the original bulk matrix elements (*e.g.*, Si) derived from the sample. Stage 2 solids represent additional opportunities for solid sampling by LA-ICP-MS, albeit at the cost of additional sample preparation steps. These transformed solids are currently under further investigation.

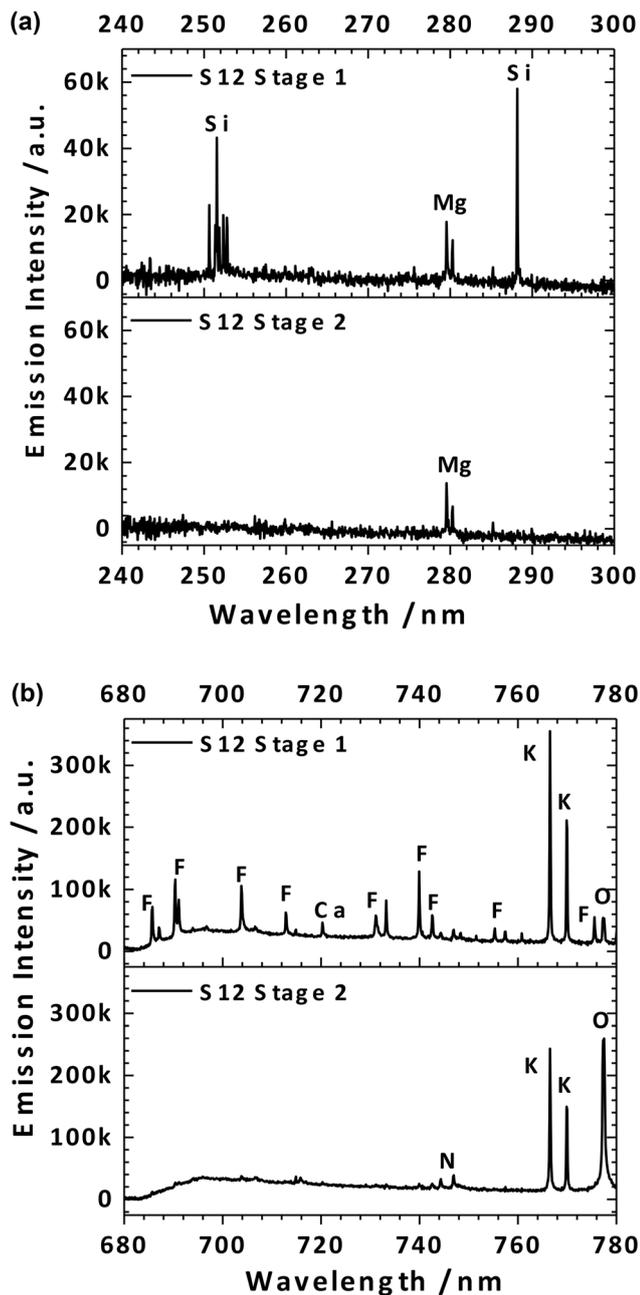


Fig. 4 LIBS spectra of Stage 1 and Stage 2 solids from the matrix transformation procedures on uranium ore S12, where (a) is a spectral window highlighting Si and (b) is a spectral window highlighting F.

Discussion

While substantial progress has been made in addressing calibration challenges in LA-ICP-MS, and these advances have been noted in recent reviews,^{1,2,4-9,23} calibration has always been a key issue and remains highly sample-dependent today. In 1996, Longerich *et al.* noted that “The major challenge to the use of laser ablation sample introduction, combined with inductively coupled plasma mass spectrometry, is the problem of calibration”,²⁴ while in 2015, Miliszkievicz *et al.* quoted Longerich

and concluded, “There are still specific issues of LA-ICP-MS that need further investigation and improvements, especially calibration procedures”.⁶ Calibration, whether internal or external, relies primarily on application specific approaches developed individually, and to date no completely universal solution to direct solids analysis calibration or matrix matching has been devised.

Here we introduce matrix transformation using reaction in molten ABF, as a means to show that it enables the addition of elemental and isotopic spikes as internal standards and tracers. The initial data here for solid matrix transformation indicate that spiked atoms are evenly distributed and that substantial improvements in precision are obtained when sample U-238 is divided by the spiked U-235. An evenly distributed isotopic tracer in a homogeneous solid would be expected to improve analysis by compensating for matrix effects and fractionation effects throughout the ablation/analysis process, as well as enabling quantification methods such as isotope dilution or standard addition.

The concept of adding internal standards into solids for quantification with LA-ICP-MS has been introduced previously, for example, with pressed powders in which liquid tracers were spiked, or powders consisting of mixtures of sample powder and tracer-containing powder.²⁵⁻³² Sometimes additional binders are included to affect the quality of the pellet or how it ablates. The matrix transformation method with ABF, introduced here, represents an additional method to enable internal calibration methods such as isotope dilution. In contrast to sample milling or pulverization, the ABF method reactively breaks down the original matrix by chemical means and enables tracer equilibration in the molten salts. Our initial studies here thus point to opportunities for solid sampling analysis with internal calibration.

In addition, matrix-matched standards may be prepared, processing standards and samples by the same matrix transformation procedure. Such standards may serve as external standards for analytical calibration, or as stable standards to track the performance of a laboratory instrument over time. A stock of standard reference materials could be built. While tremendous progress has been made in advancing laser ablation based analysis using matrix-matched and even non-matrix-matched standards,^{1,2,4-6,33-41} the opportunity to use matrix-matched standards remains the ideal and most successful approach, as it addresses many matrix-dependent physical and chemical processes. There is also the possibility of adding additional components to the transformed matrix that may influence these processes.

Looking to the future, reactive transformation using ABF, breaking down solid oxides, silicates and aluminosilicates of the original matrix, with the potential to deliberately add additional components, could lead to a common transformed matrix that can be obtained from diverse mineral samples. The approach could be similar to that used for MALDI – transforming the sample into a consistent matrix so that the laser sampling is defined by a common matrix and not by the sample itself. This also is the basis of solution analysis – the sample is a small part of the total liquid matrix introduced

into the ICP. By converting diverse mineralogical matrixes to a similar stable solid matrix, potentially diverse materials might be analyzed against a common calibration curve derived from external matrix-matched standards.

There are some reports of using high temperature fusion with lithium borate mixtures to make solid samples for LA-ICP-MS, reactively transforming the original solid sample into a new solid glass.^{41–45} Matrix transformation with molten ABF is in some ways similar to the fusion method of sample digestion, but at substantially lower temperatures and with simpler equipment. In X-ray fluorescence (XRF) fusion is particularly used to transform a solid sample to a new glass solid matrix, with opportunities to add tracers and create matrix-matched standards. Reactive transformation using ABF could potentially also be used for sample preparation for XRF or TXRF.

Although our reactions on uranium ore were bulk reactions at the 50 mg scale, the method is simple enough that it could be scaled down to very small samples sizes. Large numbers of samples can be processed in parallel. The precise mass of the transformation reagent, ABF, and hence the extent of dilution, would not be critical to analysis precision if the sample is first spiked and then analyzed by isotope dilution. For analysis of natural geological samples, the use of a U-235 spike to assess U-238 levels would be suitable. To quantify both U-235 and U-238 in processed uranium materials, another low specific activity spike such as U-233 or U-236 could be used. For elemental ratio determinations, isotopic spikes for each element could enable quantification and accurate ratio determinations. In the present initial study, laser ablation and ICP conditions have not been thoroughly evaluated for optimum conditions. We anticipate future work in investigating these parameters, and other new matrix transformed solids, with femtosecond laser ablation.^{18,19,46}

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