

## Development of CRM 125-A UO<sub>2</sub> as an Oxygen Stable Isotope Standard Reference Material

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### Abstract

The oxygen stable isotope composition of uranium oxides is emerging as a potentially powerful forensic tracer of nuclear fuel cycle materials. Stable isotope analytical techniques rely on the use of matrix-matched materials with well constrained and community established stable isotope compositions to calibrate analyses of samples. However, there are not any currently available standardized reference materials for the oxygen stable isotopic composition of uranium oxides. We collected the results of oxygen stable isotope analyses of CRM 125-A UO<sub>2</sub> Standard Reference Material from four laboratories by seven different methods. Synthesis of these data allows us to arrive at a consensus oxygen stable isotope composition for CRM 125-A  $\delta^{18}\text{O} = -9.63\text{‰} (\pm 0.29\text{‰})$  VSMOW. Contrasting analytical approaches allow us to evaluate methodological differences in fluorination agents (BrF<sub>5</sub> and ClF<sub>3</sub>), heating techniques (furnace and laser heating), and calibration strategies. We propose ways forward in the use of oxygen stable isotope compositions of nuclear materials as forensic tools.

### 1. Introduction

A goal of nuclear forensics is to be able to determine the provenance, and storage and route history of a nuclear material sample (Moody et al., 2005). For uranium oxides produced in the nuclear fuel cycle, the light stable isotopic composition (primarily oxygen) is an emerging analytical approach with great promise (Plaue, 2013; Dierick et al., 2017; Oerter et al., 2020; Klosterman et al., 2021a; Oerter et al., 2021; Assulin et al., 2021; Assulin et al., 2022). The underlying principle of the use of the oxygen stable isotope composition of uranium oxides as a forensic signature is the presence of environmental water during production processes, either as atmospheric water vapor (ambient humidity; Klosterman et al., 2022) or as precipitation-derived process water (Klosterman et al., 2021b), which is the largest reservoir of oxygen in uranium oxides. The oxygen stable isotopic composition ( $\delta^{18}\text{O}$  values, defined below) of environmental water is geospatially predictable and is well known (e.g. Dansgaard, 1964; Bowen, 2010).

The reservoir of oxygen from environmental water is likely to be integrated into uranium oxides that are either fabricated in the presence of ambient humidity (Klosterman et al., 2022) or exposed to ambient humidity during storage and transport, especially if the material is out of institutional control (Oerter et al., 2020; Oerter et al., 2021). Importantly, there are also a range of potential oxygen sources in the production process (at temperatures from 25°C to 1700°C) that may affect the resulting O isotope composition of uranium oxides. Therefore, the oxygen isotope signature of a nuclear material may enable information about the location of manufacture and its subsequent transport and storage history to be known.

The analysis of the oxygen stable isotope composition of oxides are typically made by the quantitative extraction of oxygen via fluorination with either BrF<sub>5</sub> or ClF<sub>3</sub>, which is done under vacuum at high temperature via heating by furnace or laser. The fluorination of uranium oxides for oxygen isotope analysis has been developed (Fayek et al., 1997), and is gaining increasing use (Dierick et al., 2017; Oerter et al., 2020; Assulin et al., 2021; Klosterman et al., 2021b).

The use of standardized reference materials for analytical calibrations and for inter-laboratory comparisons is a fundamental aspect of stable isotope analyses, though there are not currently any such materials for the oxygen stable isotope analysis of uranium oxides. UO<sub>2</sub> is the most prevalent uranium oxide nuclear fuel material, and thus developing a standardized UO<sub>2</sub> reference material with an established oxygen isotope composition would be of great benefit to the scientific and nuclear forensics communities. A promising UO<sub>2</sub> material is CRM 125-A Standard Reference Material (SRM) certified by New Brunswick Laboratory (Argonne, IL, USA) as a uranium concentration and isotopic assay, and as a radio-chronometric standard (U.S. DOE, 2013). The high purity and single uranium-phase of CRM 125-A is ideal for oxygen isotope analysis, thus avoiding potentially confounding effects of multiple oxygen reservoirs and allowing determination of oxygen yield with high accuracy.

This paper summarizes the results of oxygen stable isotope analyses of CRM 125-A material from four laboratories by seven different methods. We synthesize these data to arrive at a consensus oxygen stable isotope composition for CRM 125-A.

## 2. Methods

### 2.1 CRM 125-A material

CRM 125-A fuel pellets consist of 5.4 g of enriched uranium dioxide (UO<sub>2</sub>, 4% <sup>235</sup>U enrichment), which is typical of nuclear fuel used in many nuclear power plants. Each of the four laboratories participating in this study acquired their respective CRM 125-A pellets independently. From its certified uranium content ( $0.88129 \pm 0.00014$  g U•g<sup>-1</sup> pellet), the theoretical oxygen content of CRM 125-A is  $11.847 \pm 0.002$  wt.%. Before the O isotope analyses reported here, a pellet (or portion) of CRM 125-A is crushed by hand in a mortar and pestle, and the powder is homogenized in each lab to provide uniform material across repeated analyses.

### 2.3 Analytical methods

We collected oxygen isotope analyses of CRM 125-A from four laboratories, each using separate pellet aliquots of CRM 125-A. The laboratories' analytical methods are summarized in Table 1. Oxygen stable isotope values are reported in  $\delta$  notation:  $\delta = (R_{\text{sample}} / R_{\text{standard}} - 1)$ , where  $R_{\text{sample}}$  and  $R_{\text{standard}}$  are the <sup>18</sup>O/<sup>16</sup>O ratios for the sample and Vienna Standard Mean Ocean Water (VSMOW) standard.

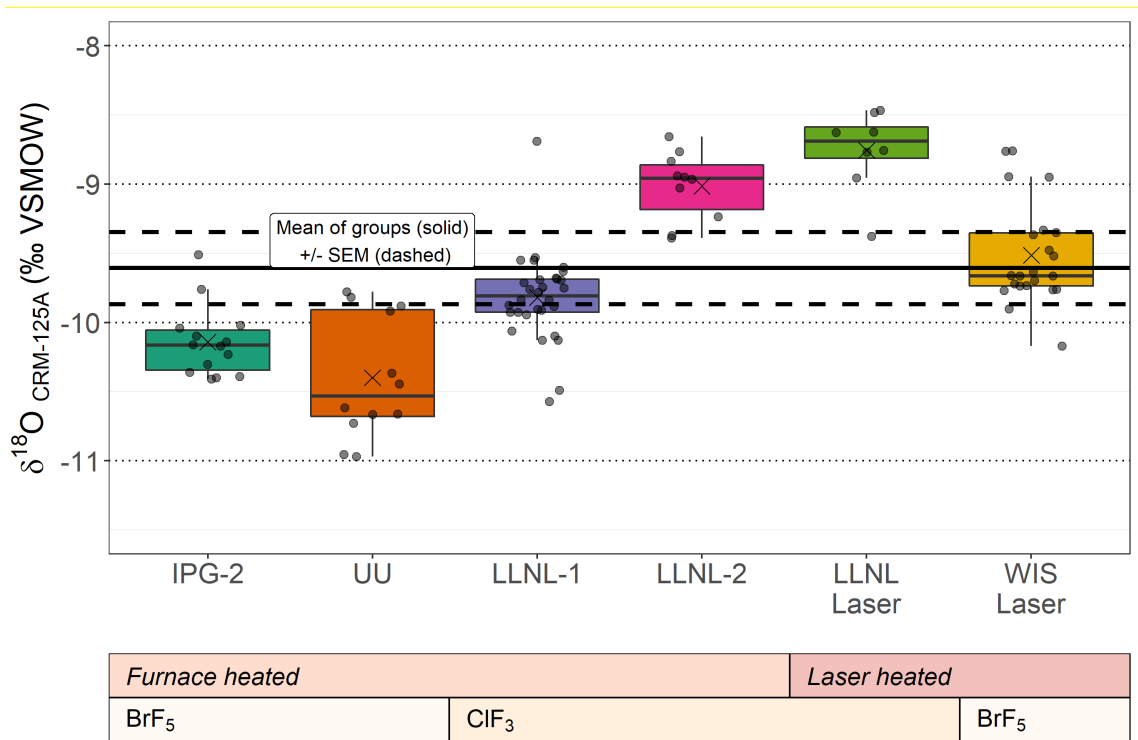
The value of oxygen isotope measurements on the VSMOW scale is dependent on the calibration of the raw measurement from the mass spectrometer to that of a reference material with

a known  $\delta^{18}\text{O}$  VSMOW value. The most commonly used silicate standard material for oxygen isotope analyses in mineral solids is NBS-28, a fine-grained quartz sand (NIST # RM-8546). To allow the comparison of datasets herein, we normalized all reported CRM 125-A  $\delta^{18}\text{O}$  data to a common reference frame based on NBS-28  $\delta^{18}\text{O}$  value of 9.58‰.

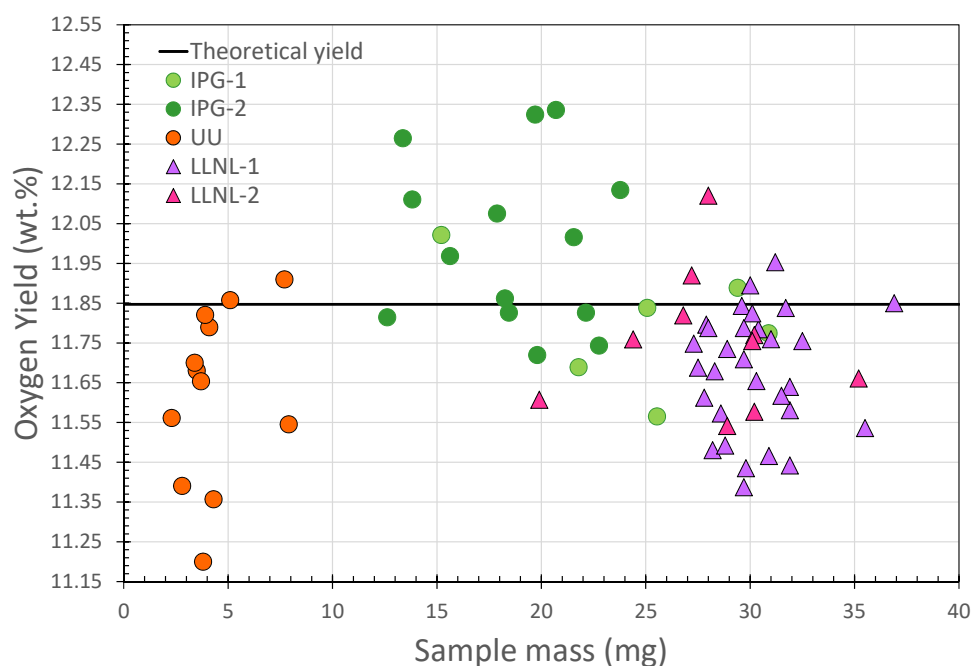
### 3. Results

#### 3.1 CRM 125-A $\delta^{18}\text{O}$ data

The oxygen isotope results on CRM 125-A are summarized in Table 1 and Figs. 1 and 2. The standard deviation of reported oxygen yields for all datasets is within 2% of the expected weight % oxygen yield from  $\text{UO}_2$  of 11.847%. The means of the CRM 125-A  $\delta^{18}\text{O}$  values of lab-datasets range from -10.82‰ to -8.76‰, and the standard deviations of the lab-datasets range from 0.12‰ to 0.44‰ (Table 1). We calculate a mean value for CRM 125-A to be  $\delta^{18}\text{O} = -9.63\text{‰}$  across all datasets (except IPG-1, discussed below) from the mean values reported for each dataset in order to not bias the mean value according to number of sample analyses within each lab-dataset (Table 1). We calculate the uncertainty of the mean value to be  $\pm 0.29\text{‰}$ , as the standard error of the mean statistic.



**Figure 1.** Box and whisker plot of  $\delta^{18}\text{O}$  values of CRM 125-A. Dataset designations follow that of Table 1. For each dataset: the middle line of the box is the median, the bottom line of the box is the lower quartile, the upper line of the box is the upper quartile, whiskers are minimum and maximum values (at most 1.5 times the interquartile range), and the  $\times$  is the mean. All data points for each dataset are superimposed on the box and whisker plot as grey dots. The overall mean of the lab-dataset groups CRM 125-A  $\delta^{18}\text{O}$  value of -9.63‰ is shown as thick black line, and dashed lines are the standard error of the mean (SEM) CRM 125-A  $\delta^{18}\text{O}$  value ( $\pm 0.29\text{‰}$ ); Oerter et al., 2022.



**Figure 2.** Plot of oxygen yield vs sample mass for analyses of CRM 125-A. Dataset designations follow that of Table 1. Oxygen yields from laser heated fluorination are not quantified during analyses and are thus not included in this figure; Oerter et al., 2022.

## 4. Discussion

### 4.1 Effects on $\delta^{18}\text{O}$ values due to differing sample analysis methods

The range of all reported results is from  $-10.82\text{‰}$  to  $-8.76\text{‰}$  (Fig. 1). The furnace-heated lab-datasets had sample sizes from 2–37 mg, prefluorination treatments from 7 to 140 torr with either  $\text{BrF}_5$  or  $\text{ClF}_3$ , preheating from 30 minutes to 12 hours, and fluorination times from 4 to 20 hours with either  $\text{BrF}_5$  or  $\text{ClF}_3$  (Table 1). IPG-1 had the lowest mean  $\delta^{18}\text{O}$  value of the furnace-heated datasets at  $-10.82\text{‰}$ , and was statistically distinguishable from all other datasets, including IPG-2 with  $\delta^{18}\text{O} = -10.14\text{‰}$ . The only difference between datasets IPG-1 and IPG-2 is the offline heating treatment (12 hr,  $150^\circ\text{C}$ , vacuum; Table 1) of IPG-2, which was designed to remove adsorbed moisture, as well as potential other oxygen-bearing volatile compounds from  $\text{UO}_2$ . While these volatiles (e.g., stearate or other lubricant from manufacturing) are likely removed by sintering at  $1700^\circ\text{C}$ , there remains a possibility that they could have exchanged oxygen during manufacturing). The difference between IPG-1 and IPG-2 highlights the potential role of the oxygen-bearing adsorbed moisture reservoir on  $\delta^{18}\text{O}$  values, and the effect of carefully removing them before reacting the sample powder in the vacuum line. Indeed, Oerter et al (2021) showed the ready hydration of  $\text{UO}_2$  in humid air, which we do not specifically account for given the range of potential lab humidity levels resulting from differing lab climates and analysis times through the year. Unfortunately, the  $\text{O}_2$  yields obtained for IPG-1 and IPG-2 cannot show the effects of the offline heating treatment, as heating happened after weighing. For the above reasons, the IPG-1 dataset is not included in the calculation of the  $\delta^{18}\text{O}$  consensus value for CRM 125-A.

For the laser-heated datasets, WIS-Laser had a mean  $\delta^{18}\text{O}$  value of  $-9.51\text{‰}$ . LLNL-Laser had a mean  $\delta^{18}\text{O}$  value of  $-8.76\text{‰}$  and was not similar to any other dataset (Table 1, Fig. 1). When evaluating differences between the two laser-heated datasets, we note that  $\text{BrF}_5$  and  $\text{ClF}_3$  have been found to be equivalent in their ability to achieve quantitative extraction of oxygen from silicates via

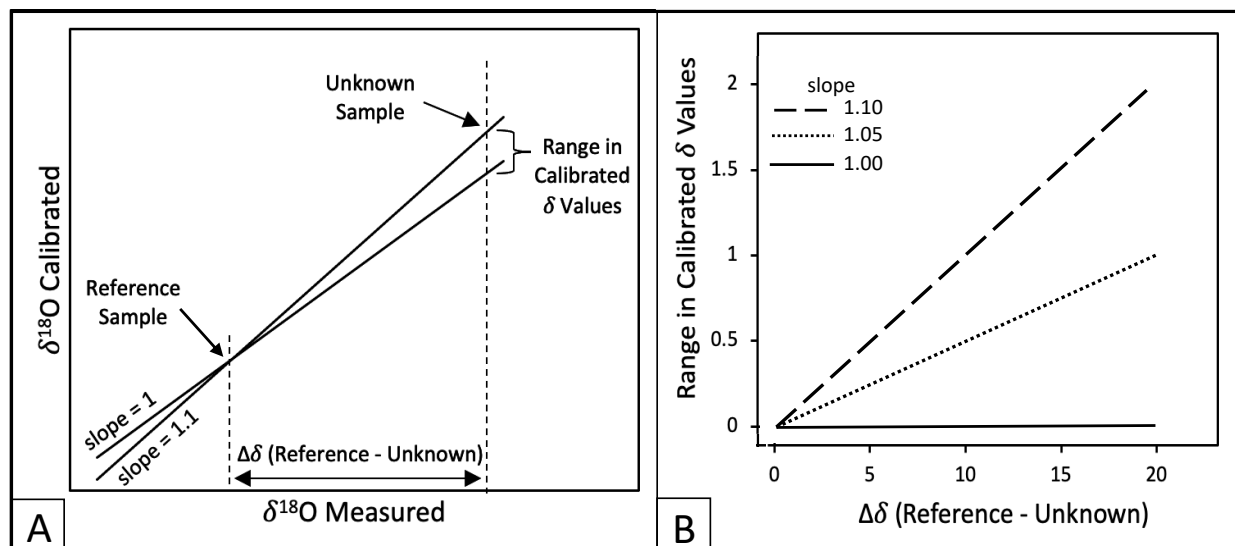
**Table 1.** Summary of compiled  $\delta^{18}\text{O}$  data on CRM 125-A. Lab datasets are designated as IPG: Institut de Physique du Globe de Paris, France; LLNL: Lawrence Livermore National Laboratory, USA; UU: University of Utah, USA; WIS: Weizmann Institute of Science, Israel. \*IPG-1 dataset not included in Consensus Value Mean calculation, see Section 4.1, NR = not reported, min = minutes, hr = hours; Oerter et al., 2022.

Lab-Dataset	Sample mass	Offline Pre-heat	Pre-fluorination	Online Pre-heat	Heating method	Gases		O Yield (% of Ideal)	Calibration to VSMOW	Normalization to NBS-28=9.58‰	CRM-125A		
						Fluorinating	Analysis				$\delta^{18}\text{O}$ ‰	St. Dev.	n
IPG-1	15–30 mg	None	100 torr, 5 min, 25 °C	120 min, 150 °C under vacuum	Furnace, 600 °C for 8 hrs	BrF <sub>5</sub>	O <sub>2</sub>	99.57 (± 1.34)	O <sub>2</sub> gas = 12.48‰	+0.30‰ (in-run NBS-28 (= 9.20‰, n=10))	-10.82*	0.12	6
IPG-2	15–30 mg	12 hr, 150 °C under vacuum	100 torr, 5 min, 25 °C	120 min, 150 °C under vacuum	Furnace, 600 °C for 8 hrs	BrF <sub>5</sub>	O <sub>2</sub>	101.30 (±1.79)	O <sub>2</sub> gas = 12.48‰	+0.27‰ (in-run NBS-28 (= 9.31‰, n=10))	-10.14	0.26	14
LLNL-1 (Pellet 1)	27–37 mg	12 hr, 150 °C no vacuum	140 torr, 5 min, 25 °C	None	Furnace, 550 °C for 4 hrs	ClF <sub>3</sub>	O <sub>2</sub>	98.57 (± 1.28)	NBS-28 = 9.58‰	N/A	-9.82	0.33	30
LLNL-2 (Pellet 2)	20–35 mg	12 hr, 150 °C no vacuum	140 torr, 5 min, 25 °C	None	Furnace, 550 °C for 4 hrs	ClF <sub>3</sub>	O <sub>2</sub>	99.20 (± 1.47)	NBS-28 = 9.58‰	N/A	-9.01	0.25	10
UU	2–8 mg	None	7–17 torr, 1-3 min, 25 °C	30–90 min, 150 °C under vacuum	Furnace, 550 °C for 16–20 hrs	BrF <sub>5</sub>	CO <sub>2</sub>	98.1 (± 1.85)	NBS-28 = 9.58‰	N/A	-10.40	0.44	12
LLNL-Laser (Pellet 1)	5–9 mg	12 hr, 150 °C no vacuum	140 torr, 5 min, 25 °C	None	Laser	ClF <sub>3</sub>	O <sub>2</sub>	NR	NBS-28 = 9.58‰	N/A	-8.76	0.30	8
WIS-Laser	1–2 mg	None	80 torr, 20 min x 3, 80 °C	~12 hr, 80 °C under vacuum	Laser	BrF <sub>5</sub>	O <sub>2</sub>	NR	NBS-28 = 9.57‰	+0.01‰	-9.51	0.37	22
Mean of 6 datasets Std Error of the Mean											-9.63	0.29	

furnace-heated fluorination (Borthwick and Harmon, 1982); however, no such comparison has been made for laser-heated fluorination, to our knowledge, and the only previous example of laser-heated fluorination using  $\text{ClF}_3$  is Akagi et al. (1995). Therefore, it is possible that the use of  $\text{ClF}_3$  in the LLNL-Laser dataset may be a factor in its mean  $\delta^{18}\text{O}$  value of  $-8.76\text{‰}$ , which is the highest of any dataset herein. The choice of fluorinating agent may have some effect as all of the LLNL datasets using  $\text{ClF}_3$  have higher  $\delta^{18}\text{O}$  values compared to the other lab-datasets which use the more traditional  $\text{BrF}_5$ , though we cannot exclude other factors.

#### 4.2 Calibration strategies

Scale compression occurs in mass spectrometric analysis as the result of instrumental mass discrimination effects and can only be corrected for by measuring two or more standard reference materials with different isotope compositions. For multi-point (MP) calibrations, more than one standard reference material is analyzed, and a line is fitted to the measured vs. known values. The slope and intercept of this best fit line are then used to correct the raw values measured on the unknown sample. A single point (SP) calibration assumes that the scale compression is negligible. Differences in the scale compression between labs and mass spectrometers could influence the  $\delta^{18}\text{O}$  value of CRM-125-A. This effect is exaggerated in the case of CRM-125-A because of its large difference in  $\delta^{18}\text{O}$  from NBS-28 ( $19.36\text{‰}$  based on the average of all methods from this study) which is used to anchor the SP calibration ( $\Delta\delta$  in Fig. 3). It is also possible that differences in the measured value of NBS-28 for the methods used in this study will directly impact the value of CRM125-A that is derived from single point calibration.



**Figure 3.** (A) Conceptual illustration of the “leverage effect” that single point calibration and compression factor slope has on calibrated  $\delta^{18}\text{O}$  values with a large difference in  $\delta^{18}\text{O}$  values ( $\Delta\delta$ ) between that of the reference sample and the unknown sample; (B) Calculated calibrated values as a function of  $\Delta\delta$  with compression factor slopes from 1.0 to 1.1. Note that compression factor slopes can also be  $<1$ , resulting in calibrated values  $<0$ ; Oerter et al., 2022.

As an example of how MP calibration improves confidence in  $\delta^{18}\text{O}$  values of CRM 125-A, LLNL used VSMOW-2 and GISP waters sealed into silver capillary tubes as calibration standards (Qi et al., 2010). While these standard waters in silver capillaries are not physically

matrix-matched to CRM 125-A, we include their use here as a demonstration of their utility. In fact, an advantage of the water standards is that they can be procured in a variety of  $\delta$  values, thus potentially more closely bracketing the unknown sample's  $\delta^{18}\text{O}$  values. In this case, VSMOW-2 ( $\delta^{18}\text{O} = 0\text{‰}$ ) and GISP ( $\delta^{18}\text{O} = -24.78\text{‰}$ ) bracket the  $\delta^{18}\text{O}$  value of CRM 125-A.

The slope of calibration lines for these MP analytical runs using water standards in silver capillaries (with and without concurrent CRM 125-A analyses) on the same fluorination system and IRMS instrument as the other analyses from LLNL presented herein is  $1.055 \text{‰} \pm 0.019$  ( $n=4$ ). The average LLNL  $\delta^{18}\text{O}$  value for NBS-28 after applying a MP calibration with the water standards run concurrently is  $9.78 \text{‰} \pm 0.32$  ( $n=6$ ), which is within uncertainty of the IAEA recommended value of  $9.58 \text{‰} \pm 0.10$  that is used here for SP calibrations. The multipoint calibration  $\delta^{18}\text{O}$  value for CRM 125-A analyzed using the furnace-heated method at LLNL is  $-10.10 \text{‰} \pm 0.21$  ( $n=4$ ), which is within uncertainty of the mean consensus  $\delta^{18}\text{O}$  value of  $-9.63\text{‰} \pm 0.29\text{‰}$  reported here. However, we see a  $0.94 \text{‰}$  difference between the LLNL corrected values for CRM 125-A when using MP and SP calibrations from the same runs, as would be expected for a scale compression equivalent to a slope of 1.055 (Fig. 3). These results suggest that differences in compression factor on the order of those shown in Figure 3 may exist between the different lab-datasets reported here, which may explain the range in reported CRM 125-A  $\delta^{18}\text{O}$  values.

#### 4.3 CRM 125-A oxygen isotope heterogeneity

The potential for O isotope heterogeneity in CRM 125-A is not directly testable with our data, though we can make inference from studies that have found CRM 125-A to be homogenous in its U isotopic composition (Krachler et al., 2014; Rolison et al., 2017), though this is not proof of O isotope homogeneity. Importantly, CRM 125-A O isotope heterogeneity is likely to be minimized by the pellets being sourced from a single production batch of  $\text{UO}_2$  fuel pellets (Kraiem et al., 2013).

Isotopic heterogeneity is most likely in small samples, such as for laser-heated and small furnace-heated analyses, if it is present. Isotopic heterogeneity between individual CRM 125-A pellets could explain some of the variability in  $\delta^{18}\text{O}$  values from different lab-datasets. Indeed, we see statistically distinct  $\delta^{18}\text{O}$  results ( $p < 0.0001$ ) between LLNL-1 and LLNL-2 which have identical methods applied to aliquots derived from two different CRM 125-A pellets (Table 1), though more analyses would be needed to confirm this. Physical homogenization of CRM 125-A is likely to be reduced during pellet grinding, and so each lab-dataset would likely not show isotopic heterogeneity. Conversely though, grinding could increase O isotope exchange with humidity in ambient air, because of increased surface area and briefly increased temperatures.

#### 4.4 Challenges when measuring the oxygen isotope value of CRM 125-A

The range of CRM 125-A  $\delta^{18}\text{O}$  values reported herein ( $-10.82\text{‰}$  to  $-8.76\text{‰}$ ), is perhaps not surprising given that the data derive from 4 laboratories on 3 different continents, and were attained by 7 different analytical methods (Table 1). As described above, such differences in calibrated CRM 125-A  $\delta^{18}\text{O}$  values may be expected for single point calibrations where the  $\delta^{18}\text{O}$  value of the SRM used to anchor the calibration is very different than the unknown sample. Commonly available SRMs with well-established  $\delta^{18}\text{O}$  values that have similar physical properties to ceramic  $\text{UO}_2$  are limited to silicates, which all have relatively high  $\delta^{18}\text{O}$  values similar to the range of NBS-28. Ideally, we can envision a synthetic glass created through closed system melting that would yield a material with similar physical properties to that of sintered

UO<sub>2</sub> materials with potentially tailorable O isotope composition to use as a standard in nuclear forensic investigations of the future.

We also see a range in oxygen yields (Figure 2) which may be attributable to oxygen being present in minor oxide phases that may form due to sample ageing in different laboratory and storage environments. Moreover, the range of reported oxygen yields may be due to differences in calibration procedures of each lab's analytical system, which is related to each system's volume and the exact temperature of each system as a whole. In general, we don't see a dependence of  $\delta^{18}\text{O}$  value on oxygen yield. We do note that some values of all the datasets have yields greater than the theoretical 100%, with no  $\delta^{18}\text{O}$  value dependence. We do not correct or remove any values from consideration of the calculated consensus mean  $\delta^{18}\text{O}$  value for CRM 125-A based on yields as the dataset average yields are close to 100% (Table 1).

We are not able to associate a systematic difference in analysis methods to a resulting range of CRM 125-A  $\delta^{18}\text{O}$  values, and therefore the variability in  $\delta^{18}\text{O}$  results may reflect properties of the material itself or challenges in calibrating results from a material with  $\delta^{18}\text{O}$  value that differs from available reference materials, as detailed below. It is known that NBS-28 powder grainsize influences laser-heated  $\delta^{18}\text{O}$  values, with smaller grains yielding lower values (Fouillac and Girard, 1996). We did not control for grainsize between lab-datasets partly because CRM 125-A is a fuel pellet material and should be shipped intact to avoid the potential for powder dispersion of radioactive material during transport. Thus, each aliquot was hand ground in each lab before analysis. In any case, a grainsize effect should be absent in furnace-heated samples.

#### *4.5 Consensus value of the $\delta^{18}\text{O}$ value of CRM 125-A*

We are not able to attribute differences in CRM 125-A  $\delta^{18}\text{O}$  values from each reported dataset to specific analytical factors that differ between laboratories, so we suggest that results from each laboratory are equally likely to be the "true"  $\delta^{18}\text{O}$  value of CRM 125-A. Therefore, towards the goal of developing a framework in which  $\delta^{18}\text{O}$  values of uranium oxides provide utility in nuclear forensics investigations, we propose the consensus value of CRM 125-A to be  $\delta^{18}\text{O} = -9.63\text{‰}$ . This consensus value is calculated as the mean value across all datasets from the mean values reported for each dataset. We calculate the uncertainty of the consensus value to be  $\pm 0.29\text{‰}$ , as the standard error of the mean statistic.

## **5. Conclusions**

The oxygen stable isotope composition of uranium oxides is of interest as a forensic signature in nuclear materials. The accurate and reliable determination of  $\delta^{18}\text{O}$  values in uranium oxides, as for any material, relies on the use of reference materials with well-established  $\delta^{18}\text{O}$  values. However, there are not any reference materials that are well-matched in terms of isotopic composition as well as physical properties for uranium oxides. In this paper we have summarized the results of oxygen stable isotope analyses (as  $\delta^{18}\text{O}$  values) from four laboratories of CRM 125-A UO<sub>2</sub> Standard Reference Material. We synthesize and discuss these data and methods to arrive at a consensus  $\delta^{18}\text{O}$  value for CRM 125-A as  $-9.63\text{‰} (\pm 0.29\text{‰})$  VSMOW. We are not able to find clear effects on CRM 125-A  $\delta^{18}\text{O}$  values of differing sample analysis methods.

This progress in the use of O stable isotopes in nuclear materials highlights several avenues for future work. We seek to highlight the potential utility of enhanced protection against ageing of sample materials through exposure to atmospheric humidity, especially those in powder form. We also suggest that Round Robin-type sample exchange and analyses would



enhance intercomparability and standardization between labs, and would ultimately foster greater collaboration between laboratories worldwide.

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