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October 13, 2021

ACS Omega

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Oxygen Isotope Fractionation in U_3O_8 during Thermal Processing in Humid Atmospheres

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ABSTRACT

The incorporation of oxygen isotopes from water into uranium oxides during industrial processing presents a pathway for determining a material's geographical origin. This study is founded on the hypothesis that oxygen isotopes from atmospheric water vapor will exchange with isotopes of oxygen in solid uranium oxides during thermal processing or calcination. Using a commonly encountered oxide, U_3O_8, the exchange kinetics and equilibrium fractionation with water vapor (in a concentration range of 50-55% relative humidity) were investigated using processing temperatures of 400, 600, and 800 °C. In an atmosphere containing only water vapor diluted in N_2, oxygen isotope equilibration in U_3O_8 occurred within 12 hours at 400 °C, and within two hours at 600 and 800 °C. Fractionation factors ($1000\ln\alpha$, $U_3O_8 - H_2O$) between the water and oxide were -12.1, -11.0, and -8.0 at 400, 600, and 800 °C, respectively. With both humidity and O_2 present in the calcining atmosphere, isotopic equilibration is attained within two hours at and above 400 °C. In this mixed atmosphere, which was designed to emulate Earth's troposphere, however, isotopes are incorporated preferentially from water vapor at 400 °C, and from O_2 at 600 and 800 °C. Rapid and temperature/species-dependent isotope exchange also elucidated the impact of retrograde exchange in humid air, showing a shift from O_2-dependent to H_2O-dependent fractionation as U_3O_8 cooled from 800 °C. These results confirm that uranium oxides inherit oxygen isotopes from humidity during thermal processing, illuminating an important mechanism in the formation of this forensic signature.

INTRODUCTION

The ubiquitous presence of oxygen bound to uranium during processing on the front end of the nuclear fuel and weapons cycles establishes a forensic significance for the stable isotopes of oxygen. Indeed, oxygen isotopes in uranium oxides have been identified in recent studies to provide information relevant to geolocation and processing history.[1, 2] In the precipitation of uranyl peroxide from water of known oxygen isotope composition, the precipitate was shown to incorporate oxygen isotopes from the aqueous solution during mineralization with a consistent fractionation.[1] When this compound was then calcined in an atmosphere of dry air, the original signature from process water was lost, and oxygen isotopes from atmospheric oxygen, O_2, were rapidly incorporated. Another study showed that in the absence of an exchanging atmosphere (i.e., inert), the thermal decomposition of ammonium diuranate between 400 and 800 °C was associated

with a consistent loss of ^{16}O.[2] While these studies highlight the potential for the use of oxygen isotopes as a forensic signature of industrially processed uranium oxides, one important atmospheric component was absent during the calcining and thermal decomposition stages—water vapor (i.e., humidity).

Water vapor can be present during many thermal processing steps in uranium production. On the front end of the fuel and weapons cycle, natural air containing a component of water vapor (at a natural concentration generally referenced by percent relative humidity, RH) may be circulated through furnaces during the calcination of yellowcakes to uranium oxides.[3] This procedure can be performed at a variety of temperatures, generally producing UO_x ($3 \leq x \leq 3.5$) below 600 °C and U_3O_8 above 600 °C.[4] The latter compound (U_3O_8) is preferred by many facilities due its enhanced transportability and reduced reactivity.[5-7] As mentioned previously, laboratory-scale experiments following oxygen fractionation during calcination in dry air have been performed which showed a rapid incorporation of oxygen isotopes from atmospheric O_2 between 300 and 1000 °C.[1] The oxygen isotope compositions found in these lab-synthesized oxides were generally more enriched in ^{18}O than samples measured from industrial facilities.[8, 9] Tropospheric oxygen has a known and globally stable isotope composition ($\delta^{18}O = +23.8 \pm 0.3‰$ vs. VSMOW: Vienna Standard Mean Ocean Water, defined below), which is significantly enriched in ^{18}O when compared to meteoric water sources (generally measured with $\delta^{18}O$ values between -30 and 0‰).[10, 11] Therefore, we hypothesize that the discrepancy in isotope ratios between laboratory and industrial oxides could be a result of the presence of humidity in industrial calcining atmospheres, which would exchange oxygen isotopes with uranium oxides at elevated temperatures causing decreased ^{18}O concentrations.

Water vapor in the form of steam is also widely utilized in fuel fabrication routes after uranium isotope enrichment of the gaseous hexafluoride (UF_6). Re-conversion of the gas back into a solid oxide is done using either a *wet* route, in which UF_6 is first dissolved into an aqueous solution prior to precipitation, or a *dry* route, in which UF_6 is hydrolyzed by steam to solid UO_2F_2. The removal of fluoride impurities from the precipitated or hydrolyzed products from either route is greatly enhanced by the addition of steam during thermal decomposition and final reduction to UO_2.[12] The presence of water vapor in these thermal processing steps again lends credence to the potential for exchange with the solid oxide, creating an oxygen isotope signature inherited from the process water. Because U_3O_8 is the intermediate product in the formation of UO_2, understanding the exchange kinetics and fractionation of the former compound with oxygen from water vapor is important.[13]

The purpose of this study was to determine first whether oxygen from water vapor (as humidity) is incorporated and exchanged with an industrially relevant uranium oxide—U_3O_8—during thermal processing or calcination. Equilibrium fractionation and exchange kinetics were investigated by calcining U_3O_8 samples in an atmosphere containing only water vapor (diluted in N_2) between 400 and 800 °C at various time intervals. Identical experiments were then conducted using a simulated industrial atmosphere, consisting of humidity with a known oxygen isotope composition diluted in dry air to determine whether a preferential or competitive fractionation occurs between water and O_2. With these new insights into the rates and extents of oxygen incorporation into uranium oxides from more practical atmospheres, a better understanding of the oxygen isotope signature in real-world nuclear materials can be formulated.

EXPERIMENTAL

Synthesis. The precipitation and structural characterization of ADU has been previously reported.[2] Briefly, ammonia was introduced into a 0.1 mol·L^{-1} solution of uranyl nitrate ($\delta^{18}O_{water}$ = -15.6‰) at 65 °C until a pH of 7.5 was attained. After a 30-minute settling period, the precipitate was filtered and washed with deionized water. The ADU was dried at 80 °C for 16 hours and then finely ground as a slurry with *n*-pentane using a zirconia mortar and pestle before storage in a vacuum desiccator.

Two separate U_3O_8 compounds were calcined from ADU which served as starting materials for aging experiments: U_3O_8_d was made by calcining ADU with vapor from H_2O_d diluted in N_2 (50-55% RH, discussed in further detail below) for 72 hours at 800 °C; U_3O_8_e was made by calcining ADU with vapor from H_2O_e diluted in N_2 (50-55% RH) for 72 hours at 800 °C. Phase purity of each U_3O_8 compound was confirmed via powder X-ray diffraction analysis using a Bruker D2 Phaser with Cu Kα X-ray source (Figure S1). Scans were performed from 10° to 90° (2θ), at increments of 0.02° and 0.5 seconds per step.

Water Samples and Equipment. Two isotopically distinct water sources were used for vapor exchange experiments: H_2O_d (liquid) with $\delta^{18}O$ = -16.47 ± 0.04‰ and H_2O_e (liquid) with $\delta^{18}O$ = +1.0 ± 0.1‰. Humidity was introduced from either of these water sources using a setup similar to that employed by Oerter et al. (2019).[14] Depending on the type of exchange experiment, either ultra-high purity (UHP) N_2 or dry compressed air (20% O_2 in N_2, $\delta^{18}O_{O2}$ = +23.2 ± 0.2‰) was diverted through two separate gas flowmeters (Across International). One flowmeter directed the gas through a 20 L carboy at 22 °C within which a 36 cm length of water vapor permeable Accurrel PP V8/2HF polypropylene membrane tubing (8.65mm outside diameter, 1.55mm wall thickness, 0.2 μm nominal porosity; Membrana GmbH, Wuppertal, Germany) was submerged. This *wet* gas line was then reconnected with a *dry* gas line emanating from the other flowmeter. The combined line was directed into a tube furnace (STF 1200, Across International). A hygrometer probe (± 5% RH accuracy; Linkstyle) was installed after the exit tubing of the furnace. Gas flowrates were kept identical for all experiments, with a 120 mL·min^{-1} flow though the *wet* line diluted with a *dry* 80 mL·min^{-1} flow. This flowrate generated a consistent relative humidity at 22 °C between 50 and 55% as measured with the outlet probe.

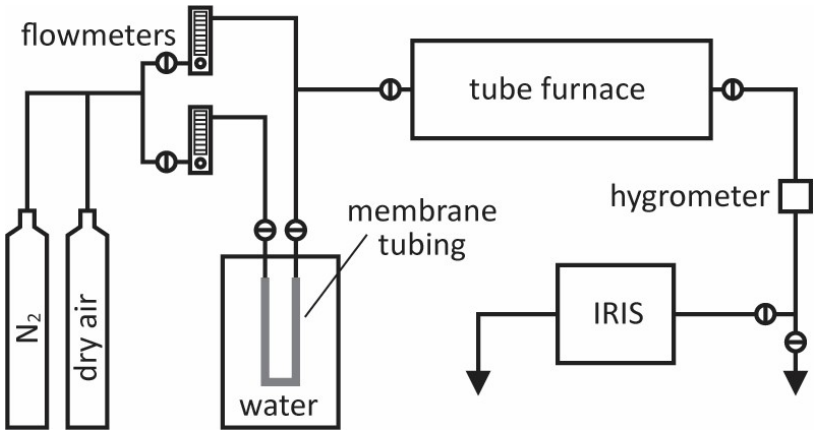

Figure 1. Setup for vapor exchange experiments. Water vapor diffuses through membrane tubing submerged in the reservoir and is subsequently diluted with a second stream of dry gas. The relative humidity is controlled by flowmeters for each gas stream.

Vapor Exchange Experiments. Before each exchange experiment, the tube furnace was equilibrated in the designated atmosphere at the designated temperature for at least 12 hours. The

first set of experiments consisted of calcining U_3O_8_d in an atmosphere of H_2O_e carried by N_2 (50-55% RH). Each U_3O_8_d starting material was split into three fractions of approximately 30-50 mg and placed in platinum crucibles. The crucibles, supported by an alumina boat, were loaded into the tube furnace at room temperature. The atmosphere in the furnace was purged for at least 30 minutes with a *wet* flow set at 120 mL·min^{-1} and *dry* N_2 flow at 500 mL·min^{-1}. The *dry* flow was then set to 80 mL·min^{-1} for approximately 30 minutes to attain a relative humidity between 50 and 55%. The furnace was then heated to 400, 600, or 800 °C at a ramp rate of 20 °C·min^{-1}. After each designated heating time interval, the *wet* flow was ceased, and the *dry* flow increased to 500 mL·min^{-1} N_2 while still at temperature. After a 10-minute flushing, the furnace was shut off and rapidly cooled (cool-down rate illustrated in Figure S2) to room temperature. Each sample replicate was weighed (to an accuracy of ± 0.1 mg) before and after each experiment to confirm the U_3O_8 had not been oxidized or hydrated (i.e., no weight change).

The second set of experiments used U_3O_8_e as the starting oxide, which was calcined in an atmosphere of H_2O_d carried by air from the dry cylinder (50-55% RH). Triplicate samples were introduced into the furnace and the atmosphere was equilibrated in the same manner as described above, with the use of air instead of N_2. After each calcination between 1 and 72 hours at 400, 600, or 800 °C, the furnace atmosphere was switched over to N_2 at 500 mL·min^{-1} and flushed for 10 minutes prior to cooling. A set of retrograde exchange experiments were also performed by calcining U_3O_8_e in H_2O_d carried by dry air (50-55% RH) at 800 °C for one hour. After the one-hour time period, the furnace was shut off and cooled either rapidly (by lifting the insulated lid) or slowly (keeping the lid closed), while the samples were still in an atmosphere of humid air (cooling rates shown in Figure S2).

Fluorination and Oxygen Isotope Measurements. Fluorination at the University of Utah was performed using a technique previously described.[1] Uranium oxide samples of 2-4 mg were loaded into Inconel reaction tubes and heated for one hour at 150 °C to remove adsorbed gases. The tubes were then prefluorinated at room temperature with 10-20 torr BrF_5 for 3 minutes before loading with 80-130 torr of BrF_5 for a 16-hour fluorination at 550 °C. Oxygen produced during fluorination was cryogenically separated from other reaction products and subsequently converted into CO_2 for offline isotope analysis. A silicate oxygen isotope standard (NBS-28, $\delta^{18}O$ = 9.6 ± 0.1‰) was fluorinated in conjunction with each set of uranium oxides for calibration.

Oxygen isotope measurements of fluorinated samples were performed within the Stable Isotope Ratio Facility for Environmental Research (SIRFER) lab at the University of Utah. Oxygen isotope ratios of CO_2 were measured using a Thermo Finnigan GasBench II device coupled to a Thermo Finnigan Delta Plus XL. The carbonate internal lab reference materials were weighed using a Sartorius microbalance, loaded into 5.9 mL flat-bottomed borosilicate vials (Labco), and capped with Labco butyl rubber septa. The vials were then flushed for 6 minutes on a PAL autosampler, with UHP helium at a flow rate of 50 mL·min^{-1}. During flushing, the vials were kept in a heated (25 °C) aluminum block. The reference materials were reacted with 10 drops of 104% phosphoric acid (kept at 25 °C) to produce CO_2 gas. The reference materials were allowed to equilibrate for 24 hours before analysis. During analysis using the PAL autosampler, CO_2 in 12 mL Labco gas vials (for both samples and reference materials) was collected using a sampling loop of 100 µL and then transported to the mass spectrometer. Five individual injections/analyses were made for each sample and reference material, and their average was taken as the final number. Three sets of internal reference materials were used to calibrate the system and for the normalization procedure to obtain isotope values for unknown samples. The reference materials were Carrara marble, LSVEC, and Marble-Std. Carrara and LSVEC were used as primary reference materials, and

Marble-Std was used as secondary reference material to cross-check the final number. Internal reference materials were calibrated against international standards NBS-18 and NBS-19.

Oxygen stable isotope values of liquid water were measured using a Picarro L2130-i laser water isotope analyzer at SIRFER, following the method demonstrated by Good et al. (2014).[15] Oxygen isotope values of water vapor produced by diffusion through membrane tubing were measured also using a Picarro L2130-i connected to the tube furnace outlet via a jacketed gas line held at 40 °C to prevent condensation. Measurements were performed with water vapor concentrations of approximately 20,000 ppmV in N_2, with a *wet* flowrate identical to that employed during aging experiments (120 mL·min^{-1}) at 23 °C.

Oxygen stable isotope values are reported in δ-notation relative to VSMOW: $\delta = (R_{Sample}/R_{VSMOW} - 1)$ x 1000‰, where R_{Sample} and R_{VSMOW} are the respective $^{18}O/^{16}O$ ratios of the sample and standard ($R_{VSMOW} = 0.00200520$),[16] and values are reported in per mille (parts per thousand, ‰). Fractionation in water between vapor and liquid is reported as 1000lnα, which is a unitless factor calculated from the quotient of $^{18}O/^{16}O$ ratios ($\alpha = R_{vap}/R_{liq}$). Fractionation between water vapor in the furnace atmosphere and U_3O_8 products is reported as either 1000lnα ($\alpha = R_{U3O8}/R_{H2O(v)}$) or $\Delta^{18}O$, representing the difference between $\delta^{18}O$ values (i.e., $\Delta^{18}O = \delta^{18}O_{U3O8} - \delta^{18}O_{H2O(v)}$). Oxygen stable isotope values of CO_2 samples were provided from SIRFER in δ-notation relative to Vienna Peedee Belemnite (VPDB) and subsequently converted relative to VSMOW using $\delta^{18}O_{VSMOW} = 1.03092\ (\delta^{18}O_{VPDB}) + 30.92$.[17] Uncertainties for $\delta^{18}O$ values of CO_2 samples and standards measured at SIRFER were generally less than 0.1‰. The uncertainty reported for each sample (1σ) was propagated from each measurement uncertainty, the literature uncertainty of the fluorination standard (NBS-28 silica, $\delta^{18}O = 9.6 \pm 0.1$‰), and the standard deviation of replicate analyses.

RESULTS AND DISCUSSION

Liquid-vapor isotope fractionation in humidity. The two distinct water vapors used for the exchange experiments were produced by diffusion of H_2O_d and H_2O_e through membrane tubing into N_2 carrier gas. The vapors were measured at 23 °C after passing through the furnace with $\delta^{18}O$ values very closely related to equilibrium values (Table 1). Fractionation (as 1000lnα, unitless) for H_2O_d vapor and H_2O_e vapors were -9.98 and -9.85, respectively, while calculated vapor-liquid fractionation at 23 °C is -9.49 based on the equation from Majoube et al. (1979).[18] The slightly larger fractionation observed among measured water vapors is likely attributable to a gas flow rate greater than the diffusion of water through membrane tubing, creating a slightly under-saturated *wet* gas stream with a higher concentration of ^{16}O.

Table 1. Measured vs. calculated $\delta^{18}O$ values (‰) for water vapors used in exchange experiments in this study. Fractionation equations from Majoube (1979) were used for equilibrium calculations.[18]

		calculated	measured	calc - meas
water	$\delta^{18}O_{liq}$	$\delta^{18}O_{vap}$	$\delta^{18}O_{vap}$	$\delta^{18}O_{vap}$
H_2O_d	-16.47 ± 0.04	-26.01	-26.2 ± 0.3	0.23
H_2O_e	+1.0 ± 0.1	-8.50	-8.8 ± 0.2	0.27

The setup employed for water vapor production in this study was modeled after that of Oerter et al. (2019), with one exception being the length of membrane tubing submerged in the water reservoir.[14] The researchers noted that isotopic equilibrium between vapor and liquid using the membrane tubing was not attained until a length of at least 200 cm was submerged. The minorly deviated fractionation in this case was expected, with a tube of only 36 cm. Nevertheless, both fractionation and water vapor concentration were consistent over experimental timeframes, with average standard deviations over 12 hours of ± 0.27‰ and ± 41 ppmV, respectively. The removal of water vapor from each reservoir during these aging experiments would be associated with Rayleigh-type fractionation, or a gradual depletion of ^{16}O in the liquid over time due to faster diffusion of the lighter isotope through the membrane tubing and into the vapor phase. Oerter et al. (2019) measured the average enrichment in $\delta^{18}O$ of water from a 19 L reservoir using a 500 $mL \cdot min^{-1}$ gas flow rate to be $0.0163‰ \cdot day^{-1}$. Given the lower flow rate used in this study (120 $mL \cdot min^{-1}$), overall experimental timeframes (approx. 15 days total use per reservoir), and similar reservoir size (20 L), the change in $\delta^{18}O$ of the vapor in these experiments was assumed to be negligible.

ADU Calcination. Ammonium diuranate used to make U_3O_8 samples for aging experiments was previously determined to have a bulk $\delta^{18}O$ value of -16 ± 1‰.[2] Calcination of this precipitate to make starting compounds for subsequent aging experiments was done at 800 °C for 72 hours in atmospheres containing either H_2O_d or H_2O_e diluted in N_2. The resulting $\delta^{18}O$ values were -43.3 and -16.7‰ for U_3O_8_d and U_3O_8_e, respectively. The seemingly unchanged isotope composition of U_3O_8_e (with respect to ADU) is a coincidental fractionation with water vapor used in the calcination ($\delta^{18}O_{H2O(v)}$ = -8.8‰). This is supported by previous work showing the calcination of this same ADU to result in a preferential loss of ^{16}O under an inert atmosphere using the same heating rate and ultimate temperature—in which case the $\delta^{18}O$ value of U_3O_8 was -0.7‰.[2]

Interestingly, fractionation factors between each of the resulting U_3O_8 compounds and the water vapor sources were different, with U_3O_8_d having $\Delta^{18}O$ = -17.1‰ and U_3O_8_e having $\Delta^{18}O$ = -7.9‰. A re-examination of the calcination procedures revealed a difference in methods; namely, termination of the calcination of U_3O_8_d was performed with water vapor still present using a slow cooling rate (see Figure S2) while the calcination of U_3O_8_e was ended by switching the atmosphere to dry N_2 prior to a fast cool-down. The difference in fractionation here was thus likely a result of retrograde isotope exchange during cooling of U_3O_8_d, a phenomenon which will be discussed in more detail in section “Retrograde Isotope Exchange”.

Fractionation with Water Vapor. Water vapor exchange experiments utilized U_3O_8_d as a starting material, which was subsequently aged between 400 and 800 °C in an atmosphere containing H_2O_e in N_2 (50-55% RH). Oxygen isotope compositions of U_3O_8 after 72 hour calcinations were taken as equilibrium values (Figure 2). Justification for equilibration within this timeframe came from a lack of statistically significant change in isotopic compositions when compared to products from shorter calcination times. At 400 °C, equilibration occurred between 2 and 12 hours because $\delta^{18}O$ values at 12 and 72 hours were identical (See Table S1 for $\delta^{18}O$ values). At and above 600 °C, isotope exchange with atmospheric humidity was fast enough that two hours was a sufficient duration for equilibration. These results show a rapid exchange between oxygen isotopes in water vapor and U_3O_8 at the temperatures utilized here.

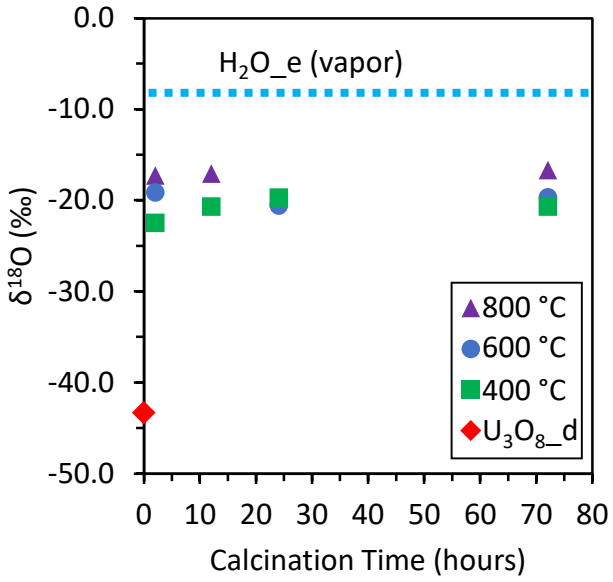

Figure 2. U_3O_8_d ($\delta^{18}O$ = -43.3‰) was calcined in an atmosphere of vapor from H_2O_e ($\delta^{18}O_v$ = -8.8‰) diluted to 50-55% RH in N_2. Samples heated at 600 and 800 °C appear to achieve equilibrium with water vapor within 2 hours, while U_3O_8 aged at the lower temperature (400 °C) reaches equilibrium between 2 and 12 hours.

As expected, higher temperature exposure led to smaller fractionation factors between U_3O_8 and water vapor. Theoretical fractionation factors for UO_3-H_2O and UO_2-H_2O from Hattori & Halas (1982) and Zheng (1991) are smaller than those measured for U_3O_8-H_2O in this work (Figure 3).[19, 20] Because U_3O_8 is a mixed-valence compound containing both U^V and U^{VI}, the bonding with oxygen, and thus fractionation, may be expected to fall between the more oxidized UO_3 and more reduced UO_2.[21, 22] The experimentally determined fractionation for U_3O_8 in this case falls well out of range of the calculations for both compounds. The greater depletion of ^{18}O in U_3O_8 here may suggest a more substantial "mass effect" (i.e., heavier elements tend to incorporate more of the light isotope and vice-versa) in uranium oxides than previously postulated.

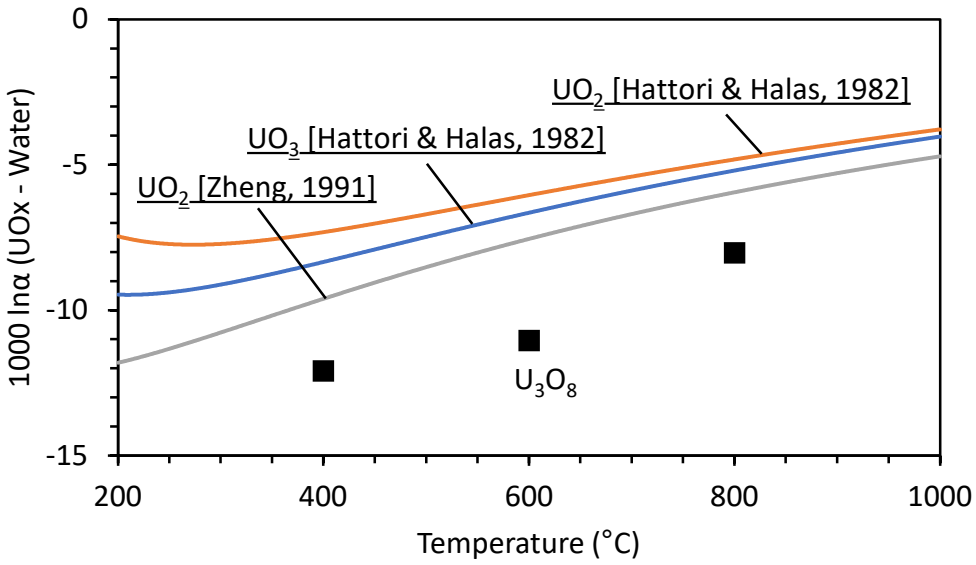

Figure 3. Oxygen isotope fractionation factors between U_3O_8 and water vapor compared to calculated fractionation for other U-oxides from equations provided by Hattori & Halas (1982) and Zheng (1991).[19, 20]

Fractionation with Humid Air. The addition of oxygen at an atmospheric concentration (i.e., 20%) to the humid calcination gas resulted in starkly different isotope fractionations among U_3O_8 products than was observed in an atmosphere containing only water vapor. When U_3O_8_e ($\delta^{18}O$ = -16.7 ± 0.5‰) was calcined in an atmosphere containing ^{18}O-depleted water vapor ($\delta^{18}O$ = -26.2 ± 0.3‰) and ^{18}O-enriched O_2 ($\delta^{18}O$ = +23.2 ± 0.2‰), fractionation was driven in opposite directions as a function of temperature (Figure 4). At 400 °C, the $\delta^{18}O$ value of U_3O_8 dropped below that of the water vapor, and was at equilibrium within two hours. In contrast, calcining at both 600 and 800 °C caused a significant increase in $\delta^{18}O$ values. Equilibration at the higher temperatures also occurred within two hours, as the $\delta^{18}O$ values from U_3O_8 products at this time interval were statistically indistinguishable from those aged for 72 hours.

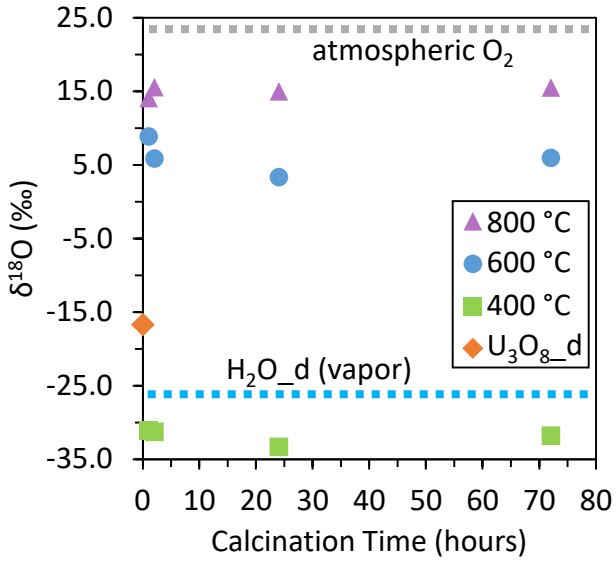

Figure 4. U_3O_8_e ($\delta^{18}O$ = -16.7‰) was calcined in an atmosphere of vapor from H_2O_d ($\delta^{18}O_v$ = -26.2‰) diluted to 50-55% RH in dry air ($\delta^{18}O_{O2}$ = +23.2‰). Samples calcined at 400, 600, and 800 °C all appear to equilibrate within 2 hours.

The different direction of fractionation observed between 400 °C and the higher temperatures suggests different mechanisms of oxygen exchange may be occurring. Previous work pertaining to corrosion and diffusion rates of oxygen in uranium and uranium oxides have illustrated temperature-dependent mechanisms. The corrosion of uranium has been shown in multiple studies to occur at different rates in the presence of water vapor, dry air, and humid air.[23-25] Haschke (1998) found that the presence of water vapor enhanced oxidation rates of uranium, except above 500 °C, where it was suggested that the reaction rates of U + H_2O and U + O_2 become indistinguishable.[24] Oxygen diffusion in uraninite has also been observed to be controlled by different mechanisms above and below 400 °C.[26]

Calcination of U_3O_8 in humid air also revealed distinct fractionations from those observed with water vapor alone or dry air (Figure 5). Although heating at 400 °C in humid air did show a water-driven isotope exchange, the $\delta^{18}O$ value was shifted more positive than the vapor-only fractionation due to the presence of O_2. Likewise, calcining at 600 and 800 °C in humid air showed a negative shift in $\delta^{18}O$ values due to the presence of water vapor. These shifts in equilibrium $\delta^{18}O$ values in the mixed atmosphere support a mechanism in which both species (H_2O and O_2) are interacting with the uranium oxide. While studies involving oxygen diffusion and reactivity of U_3O_8 in humid air at the temperatures utilized here are limited in the literature, there have been a number of investigations into the catalytic ability of the compound that may provide useful insight. Heneghan et al. (1999) found U_3O_8 to be an extremely active catalyst for the oxidation of volatile organics between 478 and 604 °C, both in the presence and absence of O_2, suggesting a redox mechanism aided by the mixed oxidation states of uranium.[27] A follow on to this work by Taylor et al. (2000) showed that isotopically labelled O_2 from the atmosphere was incorporated into oxidation products at 596 °C, which revealed that O_2 would diffuse into or onto U_3O_8 and exchange isotopes with other gaseous compounds.[28] Harris et al. (2002) then added water vapor to these catalysis experiments, which proved to be a very effective promoter for oxidation of organics by U_3O_8, making the compound active at temperatures as low as 250 °C in humid air as opposed to

350 °C in dry air.[29] Together, these studies support the interactivity between U_3O_8, H_2O, and O_2 at the temperatures used in this work, with an increasing contribution from O_2 as temperatures increase.

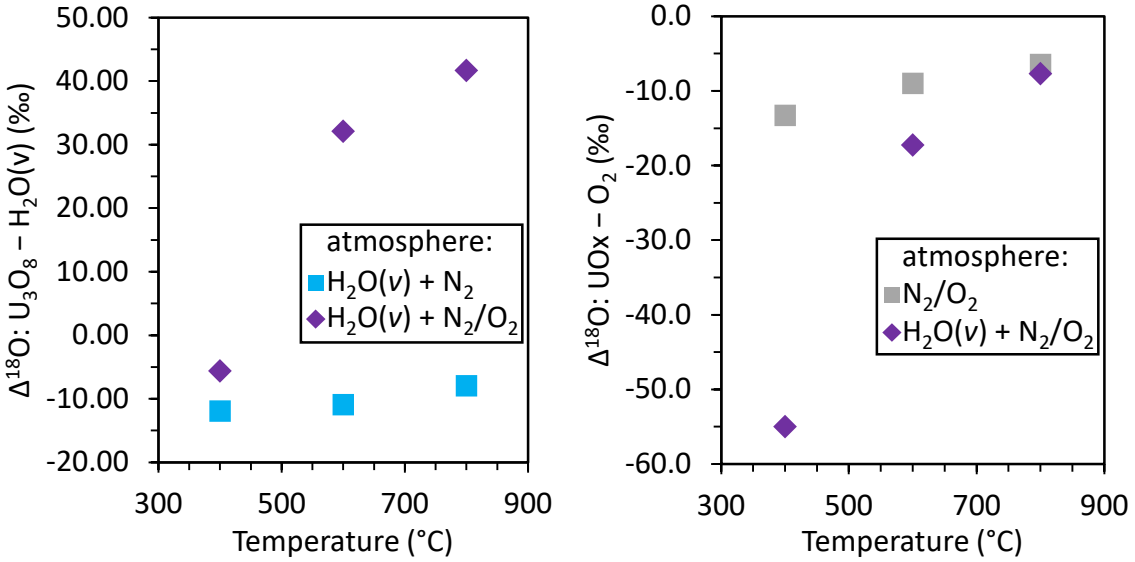

Figure 5. Fractionation between U_3O_8 and water vapor [left] and fractionation between U-oxides and atmospheric O_2 [right] during 72-hr calcining experiments. Data for fractionation between UOx and dry air (N_2/O_2, grey squares) is reproduced from Klosterman et al. (2021), with amorphous UO_3 at 400 °C and U_3O_8 at 600 and 800 °C and calcining times of 20 hours.[1]

Water vapor concentration may play a significant role in the final signature of a calcined uranium oxide. In this study, the vapor concentration during calcination experiments was kept the same (50-55% RH) throughout, as was the mass of exposed U_3O_8 (90-150 mg). With the 200 mL·min^{-1} overall flowrate employed, the exposure concentration over time for the U_3O_8 would have been between 0.21 and 0.35 mol H_2O·mol U^{-1}·min^{-1}. Given industrial settings which would maximize the throughput of solids, this exposure is likely much greater than may be encountered in calcining operations. A re-evaluation of industrial U_3O_8 samples analyzed by Plaue (2013) and Dierick et al. (2016), which had $\delta^{18}O$ values between -6.2 and +12.4‰, suggests a lack of equilibration with both atmospheric O_2 and humidity.[8, 9]

Retrograde Isotope Exchange. The combination of a temperature-dependent fractionating mechanism with rapid equilibration in the mixed atmosphere presented a potential for an additional phenomenon known as retrograde exchange. If isotope exchange kinetics at temperatures lower than the aging temperature are sufficiently fast that they exceed cool-down rates, then ultimate $\delta^{18}O$ values and fractionation will be reflective of a lower temperature. This effect was avoided in the products of calcining experiments discussed above by flushing the atmosphere with inert gas while still at the designated temperature prior to cooling. However, the potential impact of retrograde exchange is vital for a more comprehensive interpretation of the formation of oxygen isotope signatures, so the effect was investigated in this work.

As shown in Figure 5, U_3O_8 calcined for one hour in an atmosphere of ^{18}O-enriched O_2 and ^{18}O-depleted water vapor preferentially incorporated oxygen isotopes from O_2. When the atmosphere was unchanged during cooling, the products were measured with much lower $\delta^{18}O$ values, indicating incorporation of oxygen isotopes from water vapor. Both a fast cool-down rate (800 to 100 °C in approx. 20 mins) and a slow cool-down rate (800 to 100 °C in approx. 200 mins) showed significant drops in $\delta^{18}O$ values in the final product (See Figure S2 for cool-down rates). The isotope composition of rapidly-cooled U_3O_8 ($\delta^{18}O = -26.4 \pm 1.8‰$) fell directly on the water vapor line, showing a lack of retrograde equilibration over the short cooling duration, yet still a significant change from equilibrium at 800 °C ($\delta^{18}O = +14.1 \pm 0.6‰$). With a slower cooling rate, the $\delta^{18}O$ value drops below the water vapor line to $-36.3 \pm 0.1‰$, revealing a fractionation ($\Delta^{18}O$) of -12.2‰.

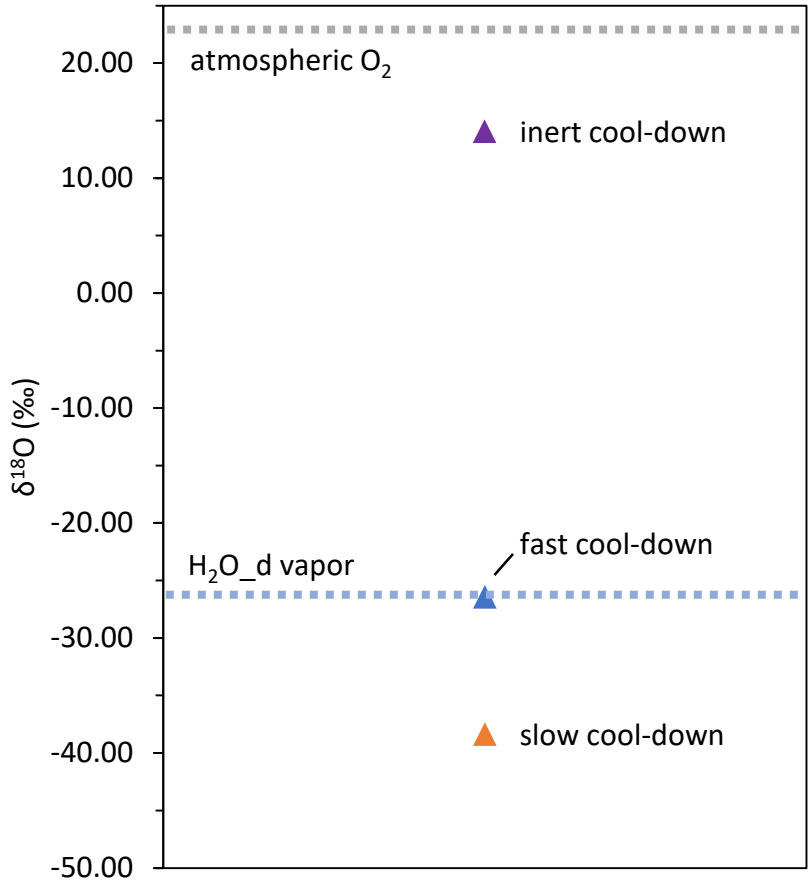

Figure 6. $\delta^{18}O$ values for U_3O_8 (initial $\delta^{18}O$ = -16.7‰) calcined for one hour in a mixed atmosphere (^{18}O-depleted H_2O vapor + air with ^{18}O-enriched O_2). U_3O_8 was cooled from 800 °C in either an inert atmosphere or the mixed atmosphere at different rates.

As mentioned previously, U_3O_8_d was made by calcination in an atmosphere with H_2O_d and slowly cooled from 800 °C with the vapor present. This led to a highly ^{18}O-depleted product having a fractionation with the water vapor of -17.1‰. This fractionation is greater than that observed

when U_3O_8 was cooled in humid air (water vapor and O_2 present), once again showing a difference in isotope incorporation and interactivity in different atmospheres. Fractionation between U_3O_8 and water vapor at 400 °C without retrograde exchange was -5.6‰ in humid air and -11.9‰ ($\Delta^{18}O$) in vapor alone; therefore, the closure temperature (i.e., temperature at which retrograde isotope exchange ceases) during this slow cooling is almost certainly lower than 400 °C.

CONCLUSION

Oxygen isotope fractionation between U_3O_8 and water vapor and between U_3O_8 and humid air was observed to occur rapidly between 400 and 800 °C, and with different mechanisms for each atmosphere. Isotope exchange with water alone led to oxides more depleted in ^{18}O than the vapor, and also more depleted than theoretically calculated fractionation factors for UO_3 and UO_2. The addition of O_2 to the humid atmosphere caused a change in the mechanism of exchange between 400 and 600 °C, with a preferential incorporation of oxygen isotopes from water at the lower temperature and O_2 at higher temperatures. The speed of isotopic equilibration in humid air also revealed the dramatic effect of retrograde exchange during cooling. While U_3O_8 incorporated oxygen from atmospheric O_2 at 800 °C, if water was still present in the atmosphere during cooling, the oxygen isotope composition of the compound was quickly altered as a result of exchange with water. These results provide novel insight into oxygen isotope fractionation in uranium oxides, and can help inform the interpretion of signatures encountered in industrial materials.

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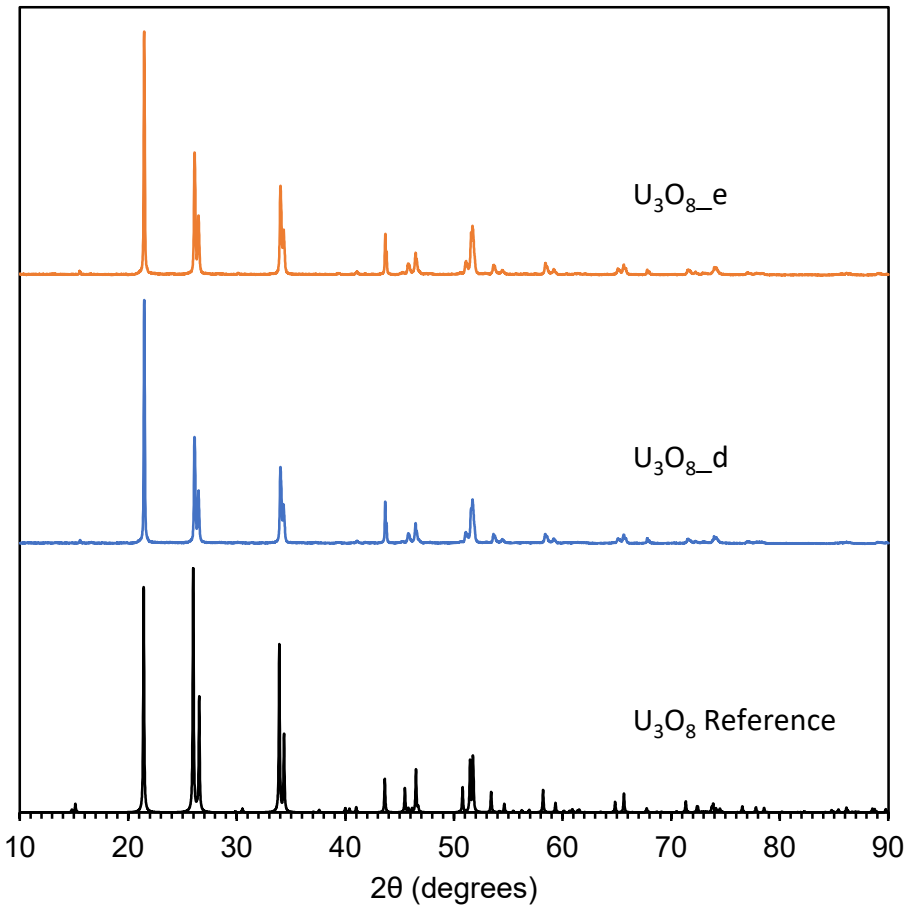

Figure S1. Powder X-ray diffraction spectra of U_3O_8 starting materials made by calcining ADU for 72 hours with vapor from either H_2O_d ($\delta^{18}O_v$ = -26.2‰) or H_2O_e ($\delta^{18}O_v$ = -8.8‰) diluted in N_2 to 50-55% RH. Reference pattern simulated from CIF files from Loopstra (1977).

Table S1. Oxygen isotope compositions for aged U_3O_8 samples and fractionation factors with atmospheric water [$\delta^{18}O(H_2O_e(v)) = -8.8‰$; $\delta^{18}O(H_2O_d(v)) = -26.2‰$] and/or atmospheric O_2 ($\delta^{18}O(O_2) = +23.2‰$).

atmosphere	temperature	time	$\delta^{18}O$ U_3O_8	$\Delta^{18}O$ U_3O_8-H_2O	$\Delta^{18}O$ U_3O_8-O_2
	(°C)	(hours)	(‰)	(‰)	(‰)
$H_2O_e(v) + N_2$	400	2	-22.5 ± 0.2	-13.7	-
		12	-20.7 ± 0.2	-11.9	-
		24	-19.7 ± 0.1	-10.9	-
	600	72	-20.7 ± 0.2	-11.9	-
		2	-19.1 ± 0.3	-10.4	-
		24	-20.6 ± 0.1	-11.8	-
	800	72	-19.7 ± 0.2	-10.9	-
		2	-17.3 ± 0.4	-8.5	-
		12	-17.1 ± 0.3	-8.3	-
		72	-16.7 ± 0.5	-7.9	-
$H_2O_d(v) + N_2/O_2$	400	1	-31.1 ± 0.3	-4.9	-54.3
		2	-31.3 ± 0.6	-5.1	-54.5
		24	-33.3 ± 0.3	-7.2	-56.5
		72	-31.8 ± 0.2	-5.6	-55.0
	600	1	8.8 ± 1.2	35	-14.4
		2	5.8 ± 1.4	32.0	-17.4
		24	3.3 ± 2.1	29.5	-19.9
		72	5.9 ± 2.0	32.1	-17.3
	800	1	14.1 ± 0.6	40.3	-9.1
		2	15.5 ± 0.2	41.7	-7.7
		24	15.0 ± 0.1	41.1	-8.2
		72	15.5 ± 0.3	41.7	-7.7

Table S2. Equilibrium $\delta^{18}O$ values and fractionation factors between U_3O_8 and water vapor.

temperature	$\delta^{18}O_{U3O8}$	1000 lnα
(°C)	(‰)	$U_3O_8 - H_2O(v)$
400	-20.7 ± 0.2	-12.1
600	-19.7 ± 0.2	-11.0
800	-16.7 ± 0.5	-8.0

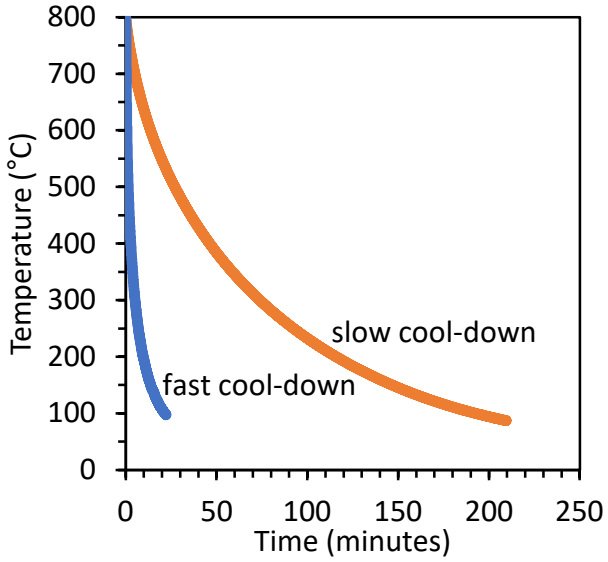

Figure S2. Cool-down rates for tube furnace. Decrease from 800 to 100 °C took approximately 20 minutes with the uninsulated (fast) cool-down and approximately 200 minutes with the insulated (slow) cool-down.