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Uranium isotope variation within vein type uranium ore deposits

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Abstract

Isotopic composition of uranium has previously been used to infer the depositional redox environment of uranium ore concentrates and also provide a potential signature to inform nuclear forensic investigations. This study evaluates the diagnostic power of the U isotope signature by investigating the (1) heterogeneity of U isotope compositions in samples collected from the same mine and/or vein, and (2) the influence of U ore processing on $^{238}U/^{235}U$ and $^{234}U/^{238}U$ ratios. These characteristics are explored via high precision mass spectrometric measurement of vein type uranium ore samples collected predominantly from mines located in central Portugal and South West England. Samples collected from the same vein and mine exhibit $\delta^{238}U$ values from −0.16 to +0.03 (± 0.04) ‰ for and $\delta^{234}U$ from −1.6 to −64.7 (± 0.4) ‰ for $\delta^{234}U$ (± 2SD). These variations can be attributed to redox-driven isotope fractionation processes and/or U redistribution during localised leaching and re-precipitation. Analyses of residues and leachates from small-scale batch experiments designed to simulate industrial U ore leaching procedures reveal significant positive and negative changes in isotope composition in the leachate relative to the bulk material (up to 0.21 ± 0.06 ‰ for $\delta^{238}U$ and 62.0 ± 0.6 ‰ for $\delta^{234}U$). These findings highlight the possibility of significantly different $\delta^{238}U$ and $\delta^{234}U$ of uranium ore concentrate from the same mine even if manufacturing processes remain unchanged.

Key Words – Nuclear Forensics, Uranium, Isotopic fractionation, Uranium ore concentrates

1 Introduction

Nuclear terrorism has been identified as one of the most serious security threats facing the world today (Kristo and Tumey, 2013). As part of the global effort to combat this issue, the International Atomic Energy Agency (IAEA) maintains a database that records incidents of illicit trafficking of nuclear and other radioactive materials (IAEA, 2006). The field of nuclear forensics concerns the analysis of such seized illicit nuclear material to infer details of its production route and origin. For such investigations, the IAEA recommends a suite of analytical tools to detect signatures in intercepted materials (IAEA, 2006), including isotopic analysis, trace elemental impurities, organic impurities, radiochronometry and morphology (Kristo et al. 2016). Here, we focus on the application of high precision uranium isotopic analysis to determine the provenance of uranium ore concentrates (UOCs).

Around 40 years ago, significantly anomalous values of the $^{238}U/^{235}U$ ratio were reported for uranium (U) ore samples collected from the ~ 2 billion years old natural fission reactors at Oklo and Bangombѐ in the Republic of Gabon, West Africa (Bodu et al. 1972). Subsequent work found that apart from these nuclear fission reactors, the $^{238}U/^{235}U$ was considered to be uniform in natural material with a value of ~ 137.84 (Cowan and Adler, 1976). In the past two decades, high precision analysis of a variety of geological samples has shown that significant $^{238}U/^{235}U$ variation at the permil-level can occur during U reduction and the exchange between U^{6+} and U^{4+} (Stirling et al. 2007; Abe et al. 2008; Weyer et al. 2008; Heiss et al. 2012; Wang et al. 2015). For instance, $^{238}U/^{235}U$ offsets of ~ 1 ‰ have been observed between tabular sandstone U deposits and high temperature magmatic deposits. It was suggested that the observed isotopic differences are induced by reduction from U^{6+} to U^{4+} during ore formation at low temperatures and that this fractionation is predominantly a natural expression of the nuclear field shift (Bopp et al., 2009; Brennecka et al., 2010; Lewis et al. 2020). This shift causes ^{235}U to be preferentially incorporated into the dissolved oxidised phase resulting in less ^{235}U in the residual reduced solid (Bigeleisen 1996). Thus, the $^{238}U/^{235}U$ fractionation due to nuclear-field shift causes relative enrichment of ^{238}U in the reduced insoluble species (mostly UO_2) and enrichment of ^{235}U in oxidised mobile species such as the uranyl ion, UO_2^{2+}, and its associated aqua complexes. Therefore, these isotope fractionation effects are also expected to be reflected in $^{238}U/^{235}U$ ratios in uranium ore minerals formed either by reduction to UO_2 or chemical precipitation in the form of U^{6+} minerals (Uvarova et al. 2014).

The mechanism causing natural variation in $^{234}U/^{238}U$ isotopic ratios differs from that of the $^{238}U/^{235}U$ system. Uranium-234 is an intermediate daughter isotope of ^{238}U decay chain to ^{206}Pb. The ^{238}U decay involves emission of an alpha-particle causing extensive damage to the mineral crystal structure. Consequently, loosely-bound ^{234}U residing in these damaged sites can be preferentially leached or directly recoiled from grain-boundaries during mineral-fluid interactions (Kigoshi, 1971). Variation in $^{234}U/^{238}U$ ratios in low temperature environments can vary by over one order of magnitude from open-system conditions (e.g. fluid alteration) showing either enrichment or depletion of ^{234}U depending on the processes of U mobility. However, any $^{234}U/^{238}U$ disequilibrium will return to equilibrium within 2.5 Ma by subsequent radioactive decay under closed-system conditions (Ivanovitch, 1992).

A range of studies have exploited both $^{238}U/^{235}U$ and $^{234}U/^{238}U$ systematics to infer the geological setting of U ore deposits (e.g. Keegan et al. 2008; Bopp et al. 2009; Brennecka et al. 2010; Uvarova et al. 2014). Brennecka et al. (2010) show that the three main types of U ore deposits (high temperature redox sensitive, low temperature redox sensitive, and non-redox sensitive) all exhibit significantly different $^{238}U/^{235}U$ values. Subsequent studies, including the analysis of further deposit types, indicated a range of 1.8 ‰ for $^{238}U/^{235}U$ (Uvarova et al. 2014). Uranium isotopic ratios are now routinely used in nuclear forensics investigation. For example, when a green radioactive powder was seized in Australia, the $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ signatures of the material were found to be consistent with UOCs from the Mary Kathleen mine (Keegan et al. 2014). Similarly, the $^{234}U/^{238}U$ value of samples taken from three active Australian mines (Ranger, Olympic Dam and Beverly) were found to be significantly different and could be used as a tool to distinguish UOC taken from each of these sites (Keegan et al. 2008). In summary, previous work has shown that $^{238}U/^{235}U$ can be utilised to infer the depositional setting of a U ore, therefore the $^{238}U/^{235}U$ signature can potentially be used predictively. However, the $^{234}U/^{238}U$ signature is expected to be site-specific because it is controlled by fluid-mediated transport, which is affected by the permeability, mineralogy and geological structure of each mineral deposit and bounding lithologies.

Although the $^{238}U/^{235}U$ signature has been used to infer U ore deposit type (Bopp et al., 2009; Brennecka et al., 2010), work by Chernyshev et al. (2014) showed significant variation, not only for minerals from individual deposits (up to 0.7 ‰), but also within single pitchblende crystals, with early growth zones enriched in ^{238}U relative the latest growth zones (Chernyshev et al., 2014). It is evident that U isotopic composition varies significantly between U ores of different deposit types, however, few studies have focused on the variation of this signature for samples collected from the same mine (e.g. Kirchenbauer et al. 2016). Uranium isotopic heterogeneity such as this could potentially mislead nuclear forensic studies that utilise U isotope ratios as key classifying features to distinguish between different types of UOC. For example, different batches of a "characterised" UOC may be produced using U ore from different extraction events. Localised U isotope heterogeneity may therefore cause different batches of UOC (from the same UOC producer) to yield an inconsistent U isotopic composition.

Furthermore, the effect of processing on the isotopic signatures of U ore has not been thoroughly tested. During processing, mined ore is crushed and pulverised to maximise the liberation of U during leaching. Depending on the deposit type and mineralogy of the ore, the size fraction may vary from 5 to 0.074 mm (IAEA, 1993). Leaching is generally carried out by the addition of sulphuric acid (low cost and widely available) with an oxidant (usually ferric iron oxide) to convert the insoluble U^{4+} to soluble U^{6+} (IAEA, 1993). Laboratory experiments have shown that during the oxidation of U^{4+} in HCl media in the presence of dissolved oxygen, the ^{238}U/^{235}U value of the remaining U^{4+} increased with time, while the ^{238}U/^{235}U of the U^{6+} product decreased (Wang et al., 2015). In addition, Stirling et al. (2007) conducted a series of sequential acid leaching experiments with single crystals of uraninite and euxenite (with radiation-damaged areas). The results indicated that mineral weathering is a possible mechanism by which ^{235}U can be fractionated from ^{238}U in ground waters (Stirling et al., 2007). Therefore, if fractionation has been observed in the natural environment and under laboratory conditions at short timescales, it is possible that processing U ore by acid leaching, which involves the transition from U^{4+} to U^{6+}, could also cause fractionation of the ^{234}U/^{238}U and ^{238}U/^{235}U ratios. If the extent of isotopic fractionation is inconsistent during conversion of uranium ore to UOC, one can expect UOCs from the same mine and processing to yield an inconsistent uranium isotope signature.

To explore potential changes in U isotopic composition in U ores and processed materials, we apply high-precision multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) U isotope measurement techniques to a suite of 42 vein type U ores from different mines, districts and regions in Portugal and South West (SW) England. Isotopic analyses of these samples are expected to build upon the previous work by Keatley et al. (2015, 2016), which focused on mineralogical and chemical data. These data are supplemented by sites situated in Niger, Namibia, Zambia and Australia. Where possible, suitable U ore samples were collected using a hierarchical approach: along the same mineral vein, within the same mine and for different mines within the region influenced by granite intrusion. A subset of the samples was leached, following industrial protocols as closely as possible at the laboratory scale, to examine changes in the isotopic composition of U during processing. The ^{238}U/^{235}U and ^{234}U/^{238}U values of the initial ore and the resulting leachate were measured to monitor for changes caused by the leaching process. All the values here are given in the form of δ^{238}U and δ^{234}U, which are calculated as follows:

$$\delta^{238}\mathrm{U} = \left[\frac{\left({}^{238}\mathrm{U}/{}^{235}\mathrm{U}\right)_{\mathrm{sample}}}{\left({}^{238}U/{}^{235}U\right)_{standard}} - 1\right] \times 1000$$

$$\delta^{234}\mathrm{U} = \left[\frac{\left({}^{234}\mathrm{U}/{}^{238}\mathrm{U}\right)_{\mathrm{sample}}}{\left({}^{234}U/{}^{238}U\right)_{sec.equilib.}} - 1\right] \times 1000$$

For δ^{238}U, the standard is CRM112A with the ^{235}U/^{238}U value equal to 137.829 (Hiess et al. 2012). For δ^{234}U, the secular equilibrium value for ^{234}U/^{238}U is 5.491×10^{-5} (Cheng et al. 2013).

2 Materials & Methods

2.1 Sample collection and preparation

Most of the U ores analysed in this study were collected from the Beiras region of Portugal and SW England, UK, with other samples from Australia, Namibia, Zambia and Niger. The Beiras region is situated in central Portugal, where hydrothermal mineral veins within the Hercynian Granites (intruded ~ 290 Ma) were mined throughout the 20th century. The region has four distinct uranium provinces (Cameron 1982a), three of which were sampled in this study; spoil heaps at eight disused mine sites from the Guarda province to the east, Roboleiro province to the north and the Urgeiriça province to the west (Cameron 1982b).

For SW England, samples were collected from 14 different mines where U mineralisation has been documented. Most of these samples were collected from spoil heaps. However, to examine isotopic heterogeneity for samples collected from within the same mine and/or the same vein, samples were taken *in situ* at Kingswood and Carbis Bay mines (Keatley et al. 2015). These samples were extracted along major zones of mineralisation in veins of the respective mines by mechanical trepanning using a hand-held drill fitted with 14-mm diamond core drill bit. Between drilling, samples and core pieces were cleaned thoroughly to avoid cross contamination. Prior to dissolution, all samples were crushed and sieved to generate a homogenised fine powder (< 63 μm).

2.2 Sample dissolution, spiking and, column chemistry

Prior to dissolution, the ^{233}U-^{236}U spike IRMM-3636 was added, aiming for a ^{238}U/^{236}U of ~150. The sample was subsequently dissolved in a mixture of concentrated HF/HNO_3/HCl acid, dried and treated with concentrated HNO_3 and H_2O_2 to oxidise residual organics. Uranium was separated from all other matrices using a UTEVA column procedure as reported in Andersen et al. (2014). In brief, the sample was dissolved in 3 ml of 3 mol/L HNO_3 and loaded onto 1 ml of UTEVA resin (Eichrom) in Teflon columns precleaned in 9 ml 0.1 mol/L HCl – 0.3 mol/L HF, 5 ml 18 MΩcm water and preconditioned in 7 ml 3 mol/L HNO_3. Matrix elements were eluted with 7 ml 3 mol/L HNO_3 followed by 3 ml 3 mol/L HCl and U collected by loading 8 ml 0.1 mol/L HCl + 0.3 mol/L HF. Samples were dried down and fluxed in concentrated HNO_3 + H_2O_2 to eliminate organics introduced during column chemistry. For measurement by MC-ICPMS, the samples were redissolved in 0.6 mol/L HCl and adjusted to a ^{238}U concentration of ~ 500 µg/L. Uranium recoveries of > 95 % were achieved via this method with total chemistry U blanks of < 20 ng.

2.3 MC-ICPMS instrument set-up

Uranium isotope ratio measurements were performed using a Thermo Finnigan Neptune MC-ICPMS at the University of Bristol Isotope Group facilities, equipped with a standard sample and X-skimmer cone. The instrument was operated in low mass resolution ($M/\Delta M \approx 450$) using an Aridus desolvating nebuliser introduction system. These conditions typically yielded U^+ transmission efficiencies of ~ 1.5 %. All measurements were made in static mode using the configuration described in Andersen et al. (2014, 2015). To set-up for $^{238}U^+$ beam intensities > 500 pA, the ^{238}U cup was connected to a feedback amplifier with a 10^{10} Ω resistor, instead of the conventional 10^{11} Ω feedback amplifier resistors. A 10^{12} Ω resistor was used for lower intensity ^{234}U beam. All other cups were connected to feedback amplifiers with 10^{11} Ω resistors. Typical ion beam intensities were ^{238}U ≈ 400 V, ^{235}U ≈ 3 V, ^{234}U ≈ 20 mV and $^{233,\ 236}$U ≈ 2 V (voltages normalised to a 10^{11} Ω resistor). These signals were integrated over a period of 80 x 4 s, while background intensities prior to measurements remained < 20 ppm of the total $^{238}U^{+}$ sample beam. Sample measurements were bracketed individually and normalised to measurements of CRM-112A spiked with IRMM-3636. Tailing and hydrides were monitored and corrected for where necessary as described in Andersen et al. (2014). Hydride formation and high-mass tailing (*m/z* 239.05/^{238}U) and the abundance sensitivity (*m/z* 237.05/^{238}U) remained stable through measurement sequences at ~ 2 – 3 x 10^{-6}. Adequate separation of Th from U eliminated the requirement to correct for $^{232}ThH^{+}$ and 1 a.m.u. high mass tailing of ^{232}Th on ^{233}U. Mass bias corrections were performed using the exponential mass fractionation law (Russell et al. 1978). Corrections were also made to account for ^{234}U, ^{235}U, ^{238}U impurities in IRMM-3636 (see Andersen et al. 2015 for further details).

During the measurement sessions internal measurement errors (± 2SE) for δ^{238}U were < 0.03 ‰ and < 0.4 ‰ for δ^{234}U (improved precision using the 10^{12} Ω resistor for the ^{234}U beam). Of the measured samples, 69 were measured two or three times. Of these, 63 samples reproduced within ± 0.03 ‰ for the δ^{238}U and all the samples were within ± 0.4 ‰ for δ^{234}U. The largest difference for two duplicated δ^{238}U measurements was 0.09 ‰ (see Supplementary Material). Detailed measurement performance using this specific set-up is described in Andersen et al. (2015). Repeated standard measurements of the standards BHVO-2 (δ^{238}U = −0.314 ± 0.028 ‰, 2SD) and inhouse CZ-1 uraninite (δ^{238}U = −0.053 ± 0.029 ‰, 2SD) gave overall external reproducibility of ±0.03‰ per individual analysis and good agreement with previously reported values for both standards. The external reproducibility of δ^{234}U are limited by low ^{234}U intensities (< 0.2 pA) but were < 3 ‰ (2 SD) for the standards and in agreement with previously reported values (Andersen et al. 2015).

To further test the accuracy of this method, a sub-set of the ten processed samples were also measured on a Nu Instruments Nu Plasma II MC-ICP-MS using a Aridus II desolvating nebulizer system at CELTIC, Cardiff University. The U isotope measurements were conducted in 0.3 mol/L HNO_3 at low mass resolution (M/ΔM ~ 400), collected in static mode with all the isotopes of interest (^{232}Th, ^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U) in Faraday cups fitted with 10^{11} Ω resistors, following the set-up in Stirling et al. (2007). General U transmission efficiencies were ~ 1 % and measurements were conducted using typical ^{238}U ion beams of ~ 4 x 10^{-10} amps with data integration over a 60 x 5 s periods, with an 0.3 mol/L HNO_3 on-peak blank measurement, subtracted from the succeeding sample measurement. Data correction and standard normalisation were similar as reported above. The internal precisions on measured δ^{238}U values are better than ±0.05 ‰ (2SE) for all samples. The external reproducibility of δ^{238}U for the in-house CZ-1 gave δ^{238}U of −0.03 ± 0.06 ‰ and −2 ± 10 ‰ for the low precision δ^{234}U measurements (2 SD, n=6) in good agreement with above measurements of the same standard at University of Bristol. For the δ^{238}U, nine out of the ten replicate measurements were reproduced within 0.06 ‰ (one sample showing 0.10‰ difference), and all the δ^{234}U were within 10 ‰ when compared to the high-precision measurements (see Supplementary Material). Based on these tests for reproducibility and accuracy, a conservative estimate of ±0.04 ‰ for δ^{238}U and ±0.4 ‰ for δ^{234}U (2SD) have been used for all the data reported in the following.

2.4 Leaching experiments

Details of industry practices for the leaching of vein type U ores were reviewed and the following experiment was designed to mimic protocols as closely as possible (Kristo et al. 2016). Uranium ore samples were ground and sieved to < 75 µm, 1 g of ore was leached in 250 ml of 0.015 mol/L (pH = 2) H_2SO_4. No additional oxidant was added but the solution was constantly agitated by a magnetic stirrer to promote ingress of atmospheric oxygen. Aliquots (5 ml) of the leachate were taken at 0.5, 1, 2, 3, 4, 5, 7, 10, 15 and 24 hours. At each leachate sampling step, temperature, pH, dissolved oxygen, conductivity, and redox potential were measured. Each aliquot was filtered using a 0.33 µm Millipore Express Millex GP filter and dried prior to separation chemistry. A total of 42 U ore samples were analysed for bulk U isotopic ratios. Of these U ore samples, isotopic measurements were performed on 17 samples following a 24-hr acid leach experiment, four samples after a 0.5-hr acid leach and seven acid-leach residues.

3 Results

3.1 Bulk samples

Measurements of bulk U ore samples exhibit a large range of δ^{238}U and δ^{234}U values. Of the 42 samples analysed (Table 1), the lowest observed δ^{238}U value (−0.63 ± 0.04 ‰) was from a torbernite ore (Guarda region of Portugal). The highest δ^{238}U value of 0.15 ± 0.04 ‰ was found in a pitchblende sample (Niger). For δ^{234}U, the most ^{234}U depleted sample (δ^{234}U = −154.6 ± 0.4 ‰) was a metatyuyamunite (Littleham Cove mine, Dartmoor, England), while the most ^{234}U enriched sample (δ^{234}U = 186.8 ± 0.4 ‰) was a tobernite ore (Reboleiro, Portugal).

Table 1: Sample information and U isotopic data for ore samples from a range of different geochemical settings, mines and veins (see supplementary material for further details on the uncertainties). The redox state is provided for those samples included in redox comparisons performed in the subsequent text.

Sample ID	Mine	Granite	Country	Uranium Mineralogy	Redox state	δ^{238}U	±2SD	δ^{234}U	±2SD
MAY_7	Botallack	Lands End	England	Bijvoetite-Y + coffinite	Reduced	-0.279	0.040	-7.5	0.4
BOT2	Botallack	Lands End	England	Uraninite, Bijvoetite-Y + coffinite	Reduced	0.050	0.040	0.9	0.4
KCB5	Carbis Bay	Lands End	England	Torbernite, Zeunerite	Oxidised	0.032	0.040	-30.6	0.4
CBJ1	Carbis Bay	Lands End	England	Torbernite, RRUP, Zeunerite		-0.330	0.040	-8.0	0.4
KCB1	Carbis Bay	Lands End	England	Torbernite, Zeunerite		-0.158	0.040	-6.6	0.4
CBJ6	Carbis Bay	Lands End	England	Torbernite	Oxidised	-0.321	0.040	24.9	0.4
KW12	Kingswood Adit	Dartmoor	England	W- Bi- Uraninite, Zeunerite, Zeunerite +W		-0.289	0.040	-64.7	0.4
KW10	Kingswood Adit	Dartmoor	England	Zeunerite		-0.175	0.040	-36.7	0.4
KW4	Kingswood Adit	Dartmoor	England	W- Uraninite, Threadgoldite, Chistyakovite, Autunite		-0.210	0.040	-1.6	0.4
LV2	Levant	Lands End	England	Bijvoetite-Y + coffinite	Reduced	-0.05	0.040	4.9	0.4
L2	Littleham Cove	Dartmoor	England	Metatyuyamunite		-0.018	0.040	-154.6	0.4
B2	Polwheveral Creek	Carmenellis	England	Iron oxide + U		0.113	0.040	-113.2	0.4
S107	Site 1	Guarda	Portugal	Torbernite	Oxidised	-0.632	0.040	-9.0	0.4
S109	Site 1	Guarda	Portugal	Saleeite, Bassetite	Oxidised	-0.070	0.040	7.5	0.4
S108	Site 1	Guarda	Portugal	Torbernite	Oxidised	0.152	0.040	-0.3	0.4
S221	Site 2	Roboleiro	Portugal	Torbernite	Oxidised	0.147	0.040	10.4	0.4
S206	Site 2	Roboleiro	Portugal	Torbernite	Oxidised	0.099	0.040	-2.5	0.4
S301	Site 3	Roboleiro	Portugal	Torbernite		-0.164	0.040	6.6	0.4
S403	Site 4	Roboleiro	Portugal	Torbernite, Zeunerite	Oxidised	-0.448	0.040	65.8	0.4
S404	Site 4	Roboleiro	Portugal	Torbernite	Oxidised	-0.302	0.040	5.0	0.4
S502	Site 5	Roboleiro	Portugal	Autunite	Oxidised	-0.217	0.040	27.8	0.4
S606	Site 6	Roboleiro	Portugal	Autunite	Oxidised	-0.472	0.040	-2.7	0.4
S601	Site 6	Roboleiro	Portugal	Phosphuranylite	Oxidised	-0.425	0.040	-3.0	0.4
S602	Site 6	Roboleiro	Portugal	Torbernite	Oxidised	-0.465	0.040	186.8	0.4
S701	Site 7	Urgeiriça	Portugal	Autunite	Oxidised	-0.305	0.040	0.0	0.4
S802	Site 8	Urgeiriça	Portugal	Autunite	Oxidised	-0.409	0.040	40.8	0.4
S804	Site 8	Urgeiriça	Portugal	Autunite	Oxidised	-0.469	0.040	26.8	0.4
S803	Site 8	Urgeiriça	Portugal	Autunite	Oxidised	-0.159	0.040	-8.5	0.4
S805	Site 8	Urgeiriça	Portugal	Autunite	Oxidised	-0.073	0.040	-10.4	0.4
STMA1	South Terras	St Austell	England	Torbernite	Oxidised	-0.145	0.040	-4.6	0.4
SAC9	St Austell Consols	St Austell	England	Pb-W-Uraninite	Reduced	0.06	0.040	1.0	0.4
WC1	Wheal Cock	Lands End	England	Bijvoetite-Y + coffinite, Coffinite	Reduced	-0.175	0.040	-9.3	0.4
LED4	Wheal Edward	Lands End	England	Torbernite, Zeunerite	Oxidised	-0.144	0.040	-0.01	0.4
OWA1	Wheal Owles	Lands End	England	Cuprosklodowskite, Uranophane	Oxidised	-0.214	0.040	35.0	0.4
OW2	Wheal Owles	Lands End	England	Bijvoetite-Y + coffinite, Uraninite, Uranophane, Coffinite		-0.52	0.040	2.0	0.4
TW1	Wheal Trenwith	Lands End	England	Pb-W-Uraninite, Torbernite, Uraninite, Zeunerite		-0.107	0.040	-99.9	0.4

WT1	Wheal Trewavas	Tregonning-Godolphin	England	Torbernite	Oxidised	-0.364	0.040	16.3	0.4
OREAS 106	-	-	Australia	-		-0.337	0.040	-8.0	0.4
Namibia	-	-	Namibia	Carnotite + Si	Oxidised	-0.458	0.040	1.5	0.4
Zambia	-	-	Zambia	Pb - Uraninite	Reduced	-0.227	0.040	0.9	0.4
Niger1	Niger 1	-	Niger	Pitchblende	Reduced	0.131	0.040	39.4	0.4
Niger2	Niger 2	-	Niger	Pitchblende	Reduced	0.293	0.040	-147.4	0.4

3.2 Changes in U isotope composition caused by acid leaching

Following a 24-hr leach in dilute sulphuric acid, we determined the difference in isotopic composition observed in the leachate relative to original bulk material (Table 2). We report this as $\Delta^{238}U_{\text{leach-bulk}}$ and $\Delta^{234}U_{\text{leach-bulk}}$:

$$\Delta^{23x}U_{\text{leach-bulk}} = \delta^{23x}U_{\text{leach}} - \delta^{23x}U_{\text{bulk}}$$

Table 2: Sample description and relative difference between bulk sample and dilute sulphuric acid leach (24 hr) for $^{238}U/^{235}U$ and $^{234}U/^{238}U$ in permil .

Sample ID	Mine	Granite	Country	Uranium Mineralogy	Redox	24hr leach–bulk (‰)			
						$\Delta^{238}U$	±2SD	$\Delta^{234}U$	±2SD
MAY_7	Botallack	Lands End	England	Bijvoetite-Y + coffinite	Reduced	0.036	0.056	-1.0	0.6
KCB5	Carbis Bay	Lands End	England	Torbernite, Zeunerite	Oxidised	-0.017	0.056	-2.8	0.6
LV2	Levant	Lands End	England	Bijvoetite-Y + coffinite		-0.008	0.056	24.3	0.6
WC1	Wheal Cock	Lands End	England	Bijvoetite-Y + coffinite, Coffinite	Reduced	-0.003	0.056	0.8	0.6
LED4	Wheal Edward	Lands End	England	Torbernite, Zeunerite	Oxidised	-0.052	0.056	8.7	0.6
OWA1	Wheal Owles	Lands End	England	Cuprosklodowskite, Uranophane	Oxidised	-0.000	0.056	-5.7	0.6
TW1	Wheal Trenwith	Lands End	England	Pb-W-Uraninite, Torbernite, Uraninite, Zeunerite	Oxidised	0.090	0.056	-62.5	0.6
WT1	Wheal Trewavas	Tregonning-Godolphin	England	Torbernite	Oxidised	0.002	0.056	-20.1	0.6
L2	Littleham Cove	Dartmoor	England	Metatyuyamunite	Reduced	0.167	0.056	-21.3	0.6
STMA1	South Terras	St Austell	England	Torbernite	Oxidised	-0.006	0.056	-30.1	0.6
SAC9	St Austell Consols	St Austell	England	Pb-W-Uraninite	Reduced	-0.035	0.056	28.6	0.6
Niger1	Niger 1	-	Niger	Pitchblende	Reduced	0.205	0.056	-3.6	0.6
S221	Site 2	Roboleiro	Portugal	Torbernite	Oxidised	0.076	0.056	-0.4	0.6
S606	Site 6	Roboleiro	Portugal	Autunite	Oxidised	-0.045	0.056	-1.8	0.6

Both positive and negative values were observed for $\Delta^{238}U_{\text{leach-bulk}}$ and $\Delta^{234}U_{\text{leach-bulk}}$ (Figure 1; Figure 2). For the SW England and Portugal samples, the largest shift in $\Delta^{238}U_{\text{leach-bulk}}$ (+0.17 ± 0.06 ‰) was sample L2 metatyuyamunite ore (Littleham Cove mine, Dartmoor, SW England), while the largest $\Delta^{234}U_{\text{leach-bulk}}$ (+62.5 ± 0.6 ‰) was observed in sample TW1 (Wheal Trenwith mine, Lands End, England). Sample S221 (Roboleiro, Portugal), is the only sample that exhibited a $\Delta^{234}U_{\text{leach-bulk}}$ that did not appear to shift from 0 (−0.4 ± 0.6 ‰). Increases in $\Delta^{234}U_{\text{leach-bulk}}$ were exhibited for SAC9 and LED4 (St Austell Consols and Wheal Edward mines), while WT1, KW4, TW1, B2, STM1A and L2 (Wheal Trewavas, Kingswood mine, Wheal Trenwith, Polwheveral Creek, South Terras and Littleham Cove) show decreases. Far fewer samples display a significant shift in $\Delta^{238}U_{\text{leach-bulk}}$; all are < 0.1 ‰, apart from Niger 1

(+0.21 ± 0.06 ‰) and the mentioned L2 metatyuyamunite. Considering the effects of the oxidation state of U in the acid leachates (Figure 2c; 2d), it is a suggestion that $\Delta^{234}U_{leach\text{-}bulk}$ is greater for mineral phases containing reduced U(IV), while the oxidised U(VI) phases exhibit a lower $\Delta^{234}U_{leach\text{-}bulk}$.

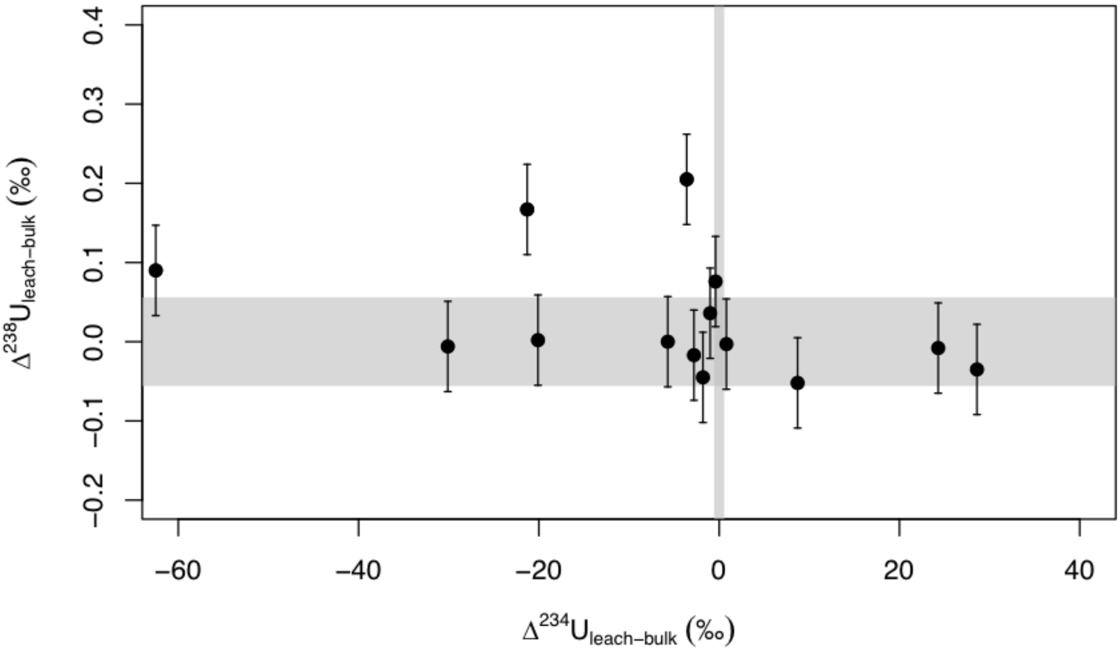

Figure 1. Relative change in isotope composition ($\Delta^{234}U_{leach\text{-}bulk}$ vs $\Delta^{238}U_{leach\text{-}bulk}$) for all samples that were exposed to a dilute sulphuric acid leach (n=14). Shaded area represents no significant change in isotope ratio (where $\Delta^{234}U_{leach\text{-}bulk} = 0 \pm 0.6$ and/or $\Delta^{238}U_{leach\text{-}bulk} = 0 \pm 0.056$).

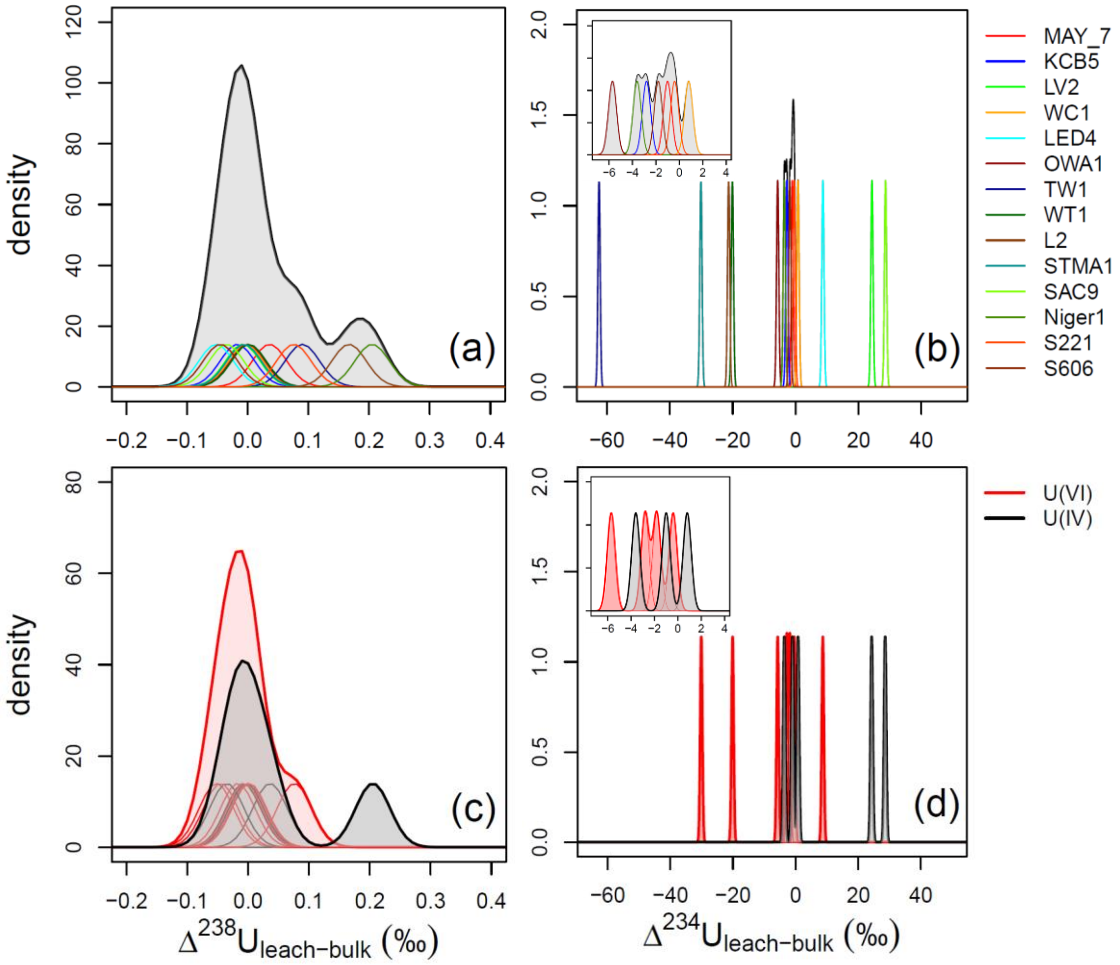

Figure 2. Relative shift in isotope composition ($\Delta^{238}U_{leach-bulk}$ and $\Delta^{234}U_{leach-bulk}$) for a selection of ores after dilute sulphuric acid leach. Shaded area represents the density plots, individual results also shown. Data for all sites (n=14) in Table 2 are colour coded in (a) and (b); subsets of data for oxidised (red) and reduced (black) U vein samples are shown in (c) and (d) (n=12).

In addition to the 24-hr leach, aliquots of 0.5-hr leachate and residue samples were collected from two oxidised (KCB5 and LV2) and two reducing (OWA1 and WC1) U phases. Leaching profiles of the uranium ores show that > 50 % U is liberated within 2.5 hours (Figure 3). The $\delta^{238}U$ for the bulk and the 24-hr leachate are similar for each of the four veins.

For $\delta^{238}U$, the residues show similar composition to the 24-hr leachate for KCB5, OWA1 and LV2, while for WC1 the residue appears to be more enriched in ^{238}U. All four samples exhibit similar $\delta^{238}U$ as the respective bulks, for the 0.5-hr and 24-hr leachates. The $\delta^{234}U$ data show some variability for the bulk and the 24-hr leachate, OWA1, WC1 and KCB5 show similar composition, while LV2 is higher. The residue of WC1 exhibits a similar $\delta^{234}U$ composition to the 24-hr leachate, while LV2 and KCB5 are lower and OWA1 is higher.

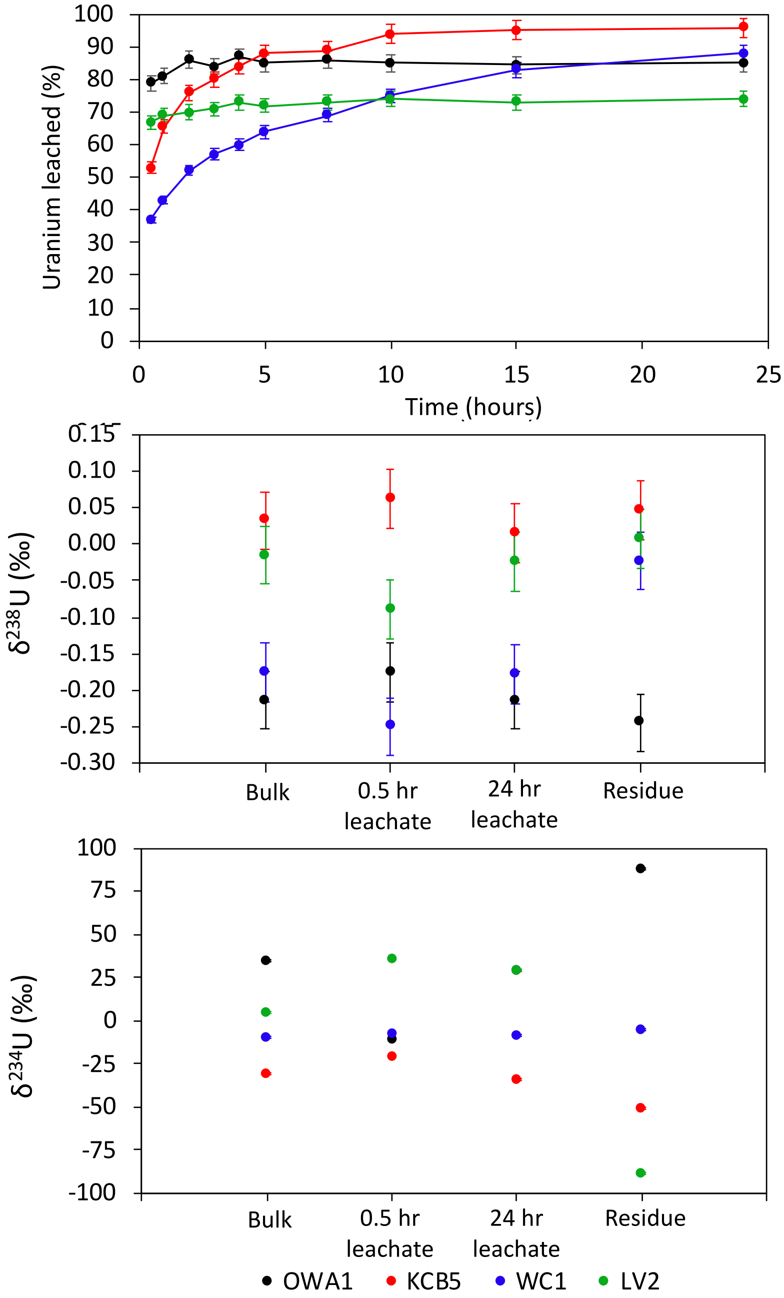

Figure 3. Leaching profiles of samples KCB5 (oxidised), WC1 (reduced), OWA1 (oxidised) and LV2 (reduced). (a) Proportion of uranium leached from ore body as a function of time. δ^{238}U (b) and δ^{234}U (c) for ore samples (bulk), the leachate produced after 0.5 hours of acid leaching, 24 hours of acid leaching and the residue remaining post-leach.

4 Discussion

4.1 Uranium isotope ratio variations in bulk samples

Since the discovery of significant natural δ^{238}U variation, several studies have analysed δ^{238}U and δ^{234}U for different types of U ore deposits. Figure 4 summarises literature data for 11 common U deposit types and associated U mineralisation. The data collected in this study broadly fits with this literature data. The mean values for the population of data obtained in this study (δ^{238}U = −0.19 ± 0.43 ‰, δ^{234}U = −6 ± 109 ‰, 2σ) are similar to mean δ^{238}U and δ^{234}U values for U vein type deposits in the literature, with δ^{234}U near secular equilibrium and the δ^{238}U similar to the average continental crust ~ −0.3‰ (Andersen et al. 2017). The range in δ^{238}U is similar, while the range in δ^{234}U measured here is larger than the compilation of the literature data for U vein-type deposits, with both higher and lower values.

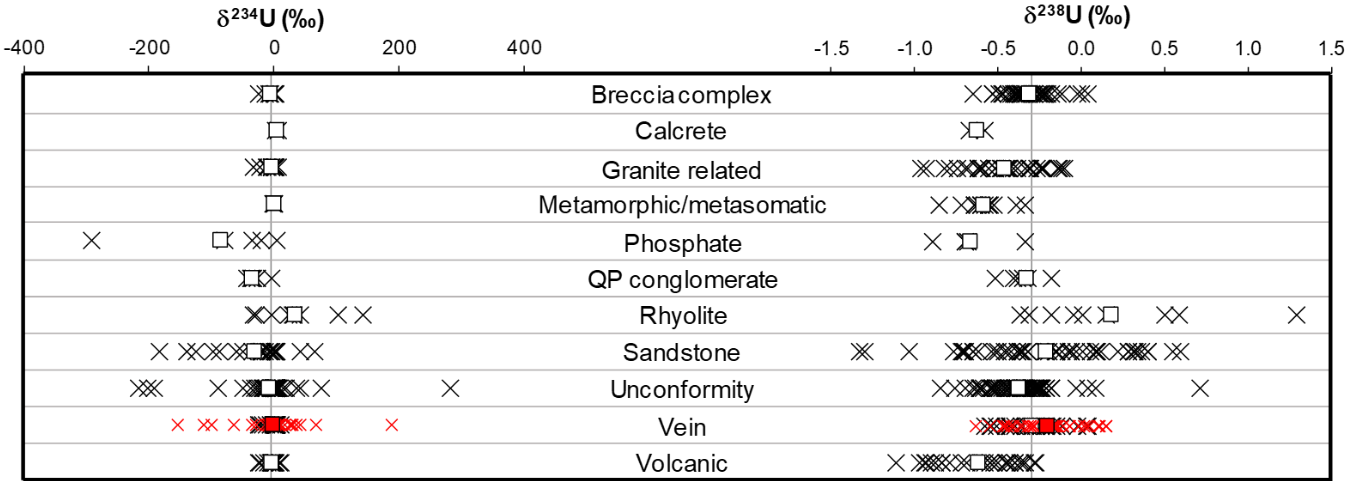

Figure 4. Variation in δ^{238}U and δ^{234}U data for uranium ore samples of different deposit types. Individual data points are plotted as crosses, mean values as squares. Data from this study is highlighted in red. Data from Brennecka et al. (2010), Uvarova et al. (2014), Kirchenbaur et al. (2016), Chernyshev et al. (2014), Bopp et al. (2009),Golubev et al. (2013), Basu et al. (2015), Keegan et al. (2008), Murphy et al. (2014). * has been renormalised with a CRM129a-CRM112a of set −1.7 instead of −0.9 permil (see Andersen et al. 2017).*

4.2 Uranium isotope ratio variations in different locations and ore types

In this study, samples from SW England and Portugal were measured for δ^{238}U and δ^{234}U (Figure 5a). There is a large overlap between the data sets for each of these settings: mean δ^{238}U values are −0.16 ± 0.33 ‰ (SW England), −0.22 ± 0.51 ‰ (Portugal); mean, δ^{234}U values are −23 ± 97 ‰ (SW England) and 10 ± 110 ‰ (Portugal). The majority of δ^{234}U values are within ± 20 ‰ of secular equilibrium, with the samples from Portugal generally exhibiting higher δ^{234}U than those from SW England. δ^{238}U overlaps for the two regions, however there is a slight trend for samples from SW England to have higher δ^{238}U in comparison to the Portuguese samples.

The δ^{238}U and δ^{234}U values may also be compared for uranium ore samples characterised by solely oxidised or reduced U bearing minerals (Figure 5b). Although these populations are not statistically different (as determined by a two-sample t-test), there is an apparent trend for the oxidised U minerals to exhibit a slightly lower δ^{238}U (no reduced minerals show $\delta^{238}\text{U} < -0.3$ ‰, while the oxidised minerals show a larger variance (0.044 compared to 0.037). The majority of the δ^{234}U values are between 50 and −50 ‰, while the oxidised minerals exhibit a more variable δ^{234}U in comparison to the reduced minerals. This is except for one reduced U mineral sample from Niger which was highly depleted in ^{234}U ($\delta^{234}\text{U} = -147 \pm 0.4$ ‰).

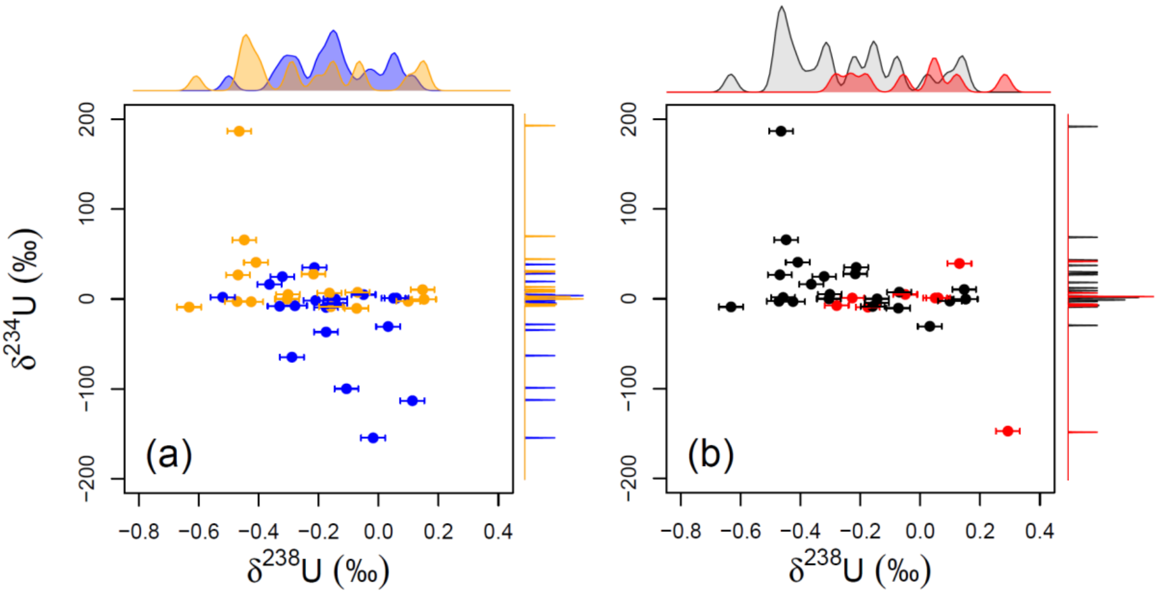

Figure 5 (a) Variation in δ^{238}U and δ^{234}U for vein deposits of SW England (blue) and Portugal (orange). (b) Plot of δ^{238}U vs δ^{234}U for samples containing only oxidised (red) and only reduced (black) uranium minerals. Probability density plots are also shown.

4.3 Uranium isotope ratio variations between different mines

The δ^{238}U and δ^{234}U signatures for the SW England and Portugal uranium ore data sets generally overlap. Indeed, after separating the samples by region, there are no clear patterns or groupings (Figure 6). This may be ascribed to the limited number of samples. Naturally, a larger suite of samples may reveal clearer trends. When plotting the samples as individual mines it is evident that there is a particularly large range in both δ^{238}U and δ^{234}U within the Lands End granite and samples from the Roboleiro district. Except for two samples from Site 6 of the Roboleiro district, samples from the same mine do not appear to have similar values.

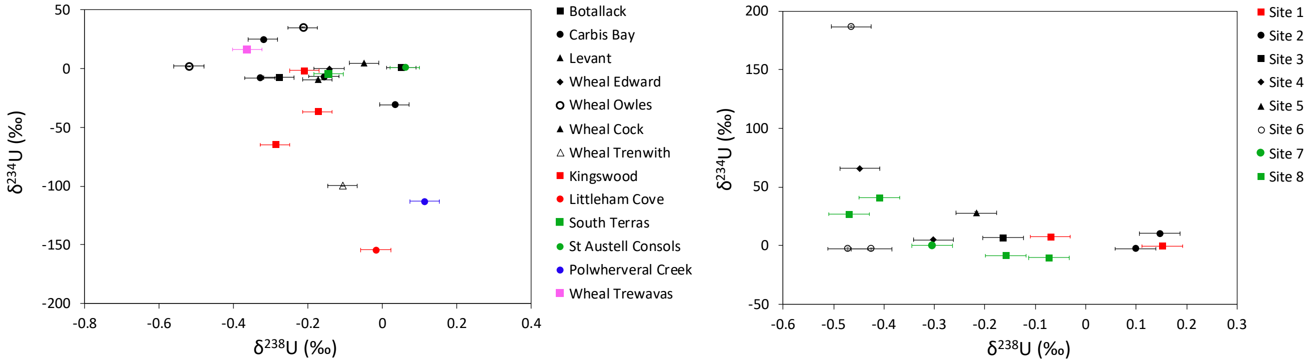

Figure 6. Plots showing the variation in δ^{238}U vs δ^{234}U values for uranium ore (colour refers to associated granite and symbols individual mines) within different districts for SW England (a) (Black = Lands End, Red = Dartmoor, Green = St Austell, Blue = Carmenelis, Pink = Tregonning-Godolphin) and Portugal (b) (Red = Guarda, Black = Reboleiro, Green = Urgeiriça).

4.4 Uranium isotope ratio variations within the same mine and vein

Variable δ^{238}U and δ^{234}U values are obtained for samples collected from along the same mineral vein at Kingswood and Carbis Bay (Figure 7). For the samples taken from three different positions along the Kingswood mineral vein, the most enriched sample in ^{238}U was KW10 (δ^{238}U = −0.18 ± 0.04 ‰), while the most depleted was KW12 (δ^{238}U = −0.29 ± 0.04 ‰). Based on single factor ANOVA, there is a significant statistical difference between these samples. Similarly, the mean δ^{234}U values are statistically different (single factor ANOVA), and decrease along the mineral vein. The most enriched sample in ^{234}U along the Kingswood vein was KW4 (δ^{234}U = −1.5 ± 0.4 ‰) and the most depleted was KW12 (δ^{234}U = −64.7 ± 0.4 ‰).

Two samples were collected from the start and end of two veins (KCB and CBJ) within 10 m of one another from a mine at Carbis Bay (Figure 7c; 7d). Although uncertainties overlap at the 95 % confidence level, two sample t-tests (significance level, α, of 0.05) show that there is a statistical difference in the mean δ^{238}U values for the two samples from vein CBJ (CBJ1 = −0.35 ± 0.04 ‰, CBJ6 = −0.32 ± 0.04 ‰). Additionally, the δ^{238}U for the samples from vein KCB show greater variability (KCB1 = −0.16 ± 0.04 ‰, KCB5 = +0.030 ± 0.04 ‰) (Figure 7c). The δ^{234}U for the two samples collected from each of the two veins at Carbis Bay are statistically different (CBJ1 = −16.0 ± 0.4 ‰, CBJ6 = 24.9 ± 0.4 ‰; KCB1 = −6.6 ± 0.4 ‰, KCB5 = −30.6 ± 0.4 ‰). In summary, these measurements show evidence of a heterogeneous U isotopic composition (for both δ^{234}U and δ^{238}U) for samples collected from within the same mine and from the same vein.

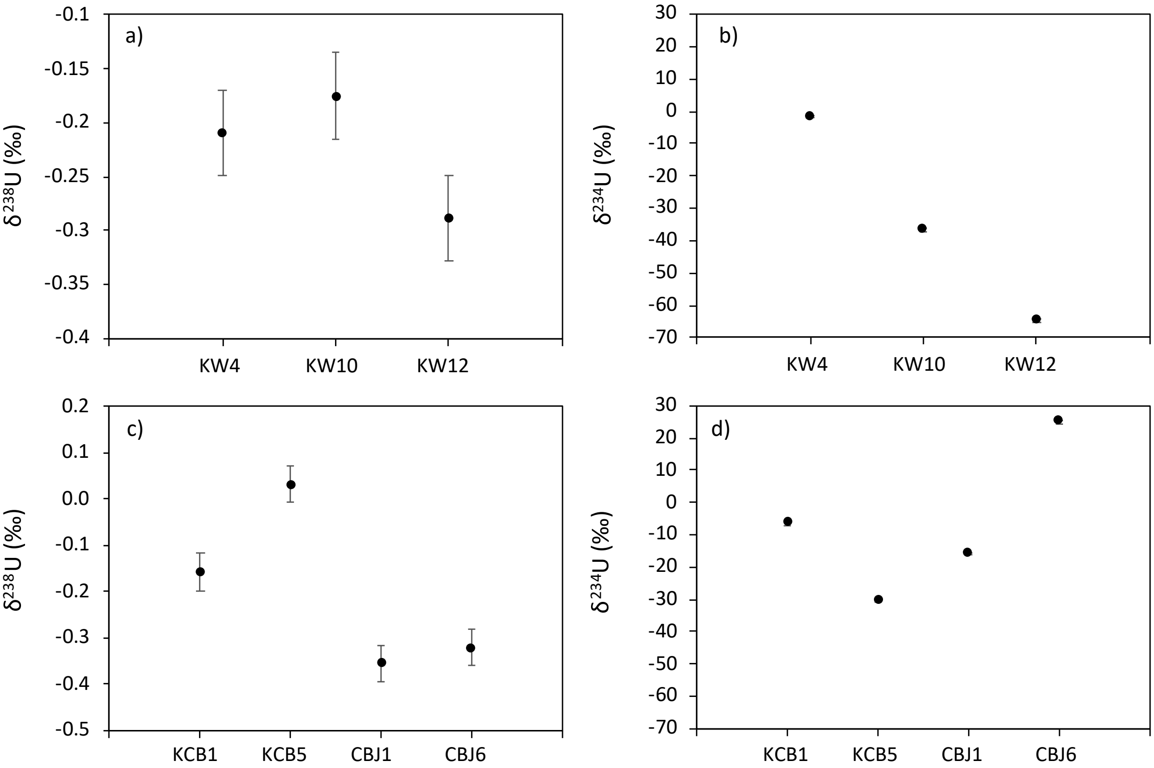

Figure 7. Variation in δ^{238}U vs δ^{234}U within the Kingswood mineral vein (a, b) and the two Carbis Bay mineral veins (c, d). Typical uncertainties for δ^{234}U are smaller than the marker.

4.5 Processes responsible for the uranium isotope ratio variations

Here we discuss the specific U isotope signatures in the samples analysed, focusing firstly on mechanisms that influence δ^{234}U and then δ^{238}U.

4.5.1 δ^{234}U signatures in the vein ore minerals

One key observation is that most of the bulk samples analysed are in a state of U-series disequilibrium (δ^{234}U deviating from 0). The samples with oxidised U minerals are determined to be more variable and exhibit higher δ^{234}U, whereas samples with reduced U minerals show less variability and more samples with δ^{234}U < 0 (Figure 5b). Disequilibrium in ^{234}U/^{238}U has been associated with localized crystal damage induced by α-recoil processes and can be achieved in several ways in uranium-rich ore samples, both from physical redistribution at steady-state and from non-steady state chemical weathering processes. In a heterogeneous sample containing phases with different U concentrations, α-recoil processes may re-distribute ^{234}U across grain boundaries from high to low U phases, leading to δ^{234}U below and above 0 in each medium, respectively. This process may occur at steady-state, thus being independent of the decay rates and time. In this scenario, the high U-containing mineral phases, as sampled in this study would be expected to exhibit δ^{234}U values < 0. This could explain some of the observed data, but not the samples with δ^{234}U above secular equilibrium. Thus, the data suggests that the observed disequilibrium is likely associated with more recent weathering-driven U mobility. Preferential mobility of ^{234}U during oxidative weathering and leaching, generally leads to a residue below secular equilibrium and excess ^{234}U in a dissolved form. In addition, adsorption of ^{234}U to mineral phases (e.g. via the short-lived ^{234}Th daughter), provides one mechanism for samples to obtain δ^{234}U > 0. Reprecipitation of U minerals from dissolved U-rich geofluids, with excess ^{234}U from U vein leaching, provides an alternative mechanism. These observations suggest that the variable δ^{234}U in the U ores is likely linked to recent (< 2.5 Ma) processes of U mobility associated with the redistribution of U daughter isotopes from within the ore systems. This trend may explain the characteristic difference between the Portuguese and English U vein samples. All Portuguese samples are secondary minerals. Therefore, it is possible that the excess ^{234}U in many of these samples is a result of secondary mineralisation of U leached from a primary ore with a high δ^{234}U. Furthermore, relatively low rainfall, as occurring in the regions of the Portuguese samples, promotes high δ^{234}U in the dissolved U fluids via increased residence times and water-rock interaction (Robinson et al. 2004). In contrast, the SW England samples may represent older primary uranium phases where ^{234}U has been preferentially leached and therefore generally lower δ^{234}U. Indeed, this suggestion is strengthened by the observation that these SW England samples were sourced from tailings piles and old mine adits (>100 years old) that have been continuously leached by meteoric waters.

Δ^{234}U$_{\text{leach-bulk}}$ also varies considerably between the majority of leachates relative to the bulk (Figure 1; Figure 2; Figure 3). Some of the reduced U minerals show an excess of ^{234}U in the leachates, which could be attributed to preferential release of ^{234}U from damaged crystal lattice sites. The oxidised U ores, however, generally show lower ^{234}U in the leachates than the bulk, which suggest limited preferential release of ^{234}U and incongruent dissolution of areas with lower δ^{234}U (e.g. near grain boundaries). Taken together it suggests that the reduced U minerals are generally of older origin and susceptible to preferential release of ^{234}U, while the majority of the oxidised U minerals are likely precipitated from U-rich fluids as secondary phases produced from weathering processes via U vein dissolution within the vein system.

4.5.2 $\delta^{238}U$ signatures in the vein ore minerals

The U ores samples show a large variability of ~ 1 ‰ in $\delta^{238}U$ (Figure 4). The reduced U mineral samples range from the average crustal value (−0.3 ‰) and to higher values (+0.3 ‰), while the oxidised U minerals are similarly high, but extend to lower compositions (−0.6 ‰). The overall lower $\delta^{238}U$ for the oxidised U minerals relative to the reduced U mineral samples agrees well with the expected U isotope fractionation during U redox transformations, favouring the ^{238}U in the reduced U^{4+} phases (Bigeleisen, 1996). The cause of the similar $\delta^{238}U$ observed for oxidised and reduced U minerals is analogous to an interpretation applied to $\delta^{234}U$: the oxidised U minerals are secondary phases derived from the oxidation and dissolution of reduced U minerals in a different part of the ore system. Experimental studies have shown only minor U isotope fractionation (< 0.2 ‰) for the oxidation of uraninite minerals (Wang et al. 2015) which fits with the similar, but slightly lower $\delta^{238}U$ for the oxidised U minerals. The minor variability in $\delta^{238}U$ for some leachates relative to the bulk (Figure 1; Figure 2; Figure 3), may indicate isotope fractionation or artifacts from re-adsorption processes during this leaching (Wang et al. 2015) or the dissolution of discrete areas or phases with different $\delta^{238}U$ (Chernyshev et al., 2014). While the both the oxidised and reduced U mineral samples show an increase in $\Delta^{238}U_{\text{leach-bulk}}$ (Figure 2), the progressive leaching studies (Figure 3) show no systematic change in $\Delta^{238}U_{\text{leach-bulk}}$ for any of the samples. Thus, it is likely that the variable $\Delta^{238}U_{\text{leach-bulk}}$ are from a combination of the two above processes (isotope fractionation during leaching/absorption and pre-existing sample heterogeneity).

4.6 Implications for nuclear forensics

Isotopic measurements of uranium materials have been successfully deployed in nuclear forensics investigations as comparative signatures to determine the provenance UOCs out of regulatory control. The methodology compares material characteristics of a seized sample of unknown origin to a database of previously characterised samples of known origin. This allows direct attribution or in the least, ruling out specific material sources. In addition to utilising the U isotopic composition as a forensic indicator, other distinguishing material characteristics may include, the major molecular species, isotopic composition of S, O, Sr, Nd, Mo and Pb, elemental and anionic impurities, rare earth element pattern and concentrations (Han et al. 2013; Keegan et al. 2014; Rolison et al. 2019; Migeon et al. 2020). This equates to approximately 50 discrete signature variables. A range of statistical tools may subsequently be used to relate the unknown material to a characterised database sample (Keegan et al. 2012;

Corcoran et al. 2019). Although δ^{234}U and δ^{238}U may only represent two of these 50 potential variables, they have previously been recognised as key comparative discriminators (Keegan et al. 2016). It is therefore important for the nuclear forensics practitioner to acknowledge potential perturbation of these signatures based on observations made in this study: localised isotopic heterogeneity and changes in the U isotope composition caused by a weak sulphuric acid leach.

If the uranium isotope ratios remained unchanged during processing of ore to UOC, the data suggest that taken broadly, the δ^{238}U reflect the ore's original depositional setting (e.g. depositional redox conditions) allowing individual deposit types to be separated. The δ^{234}U is regarded as being site specific and will depend on several conditions e.g. water-rock interaction history within the last 1-2 million years will be linked to the age, permeability and structure of the deposit. Therefore, δ^{238}U and δ^{234}U may be deployed as separate nuclear forensic signatures; δ^{238}U predictively, whereas δ^{234}U is more site specific (Brennecka et al., 2010).

The experiments here demonstrate uranium isotope heterogeneity for samples collected from the same mine, albeit on an extremely small sample scale (~ 1 g) relative to industrial scale ore extraction. Based on the relatively large variability in these samples and within single mines, isotopic heterogeneity may be expected regardless of the amount of ore extracted. There is no evidence to suggest that sampling a sufficiently large quantity of ore may yield a non-variable uranium isotope ratio that is representative of the respective mine. Therefore, if different batches of UOC have been produced by a processing facility using uranium ore from different extraction events at the same mine, it is not necessarily valid to assign a fixed value for the uranium isotopic composition of a UOC.

Following dilute sulphuric acid treatment to simulate industrial ore processing, significant differences between the δ^{238}U values of bulk solid (ore) and leachate (processed material) were observed for a limited number of samples in this study, and for δ^{234}U this was the case for nearly all samples (Figure 1). This contrasts with results of a study comparing two uraninite specimens (feed material) to four samples of product UOC material from the Willow Creek Project (South Powder River Uranium district, Wyoming) for which ^{238}U/^{235}U and ^{234}U/^{238}U remained broadly consistent (Spano et al. 2017). Based on these findings, the study concluded that any changes to the U isotopic signature caused during early ore processing were insignificant. It is possible that different conclusions have been reached because of the limited number of samples and single location studied in Spano et al. 2017.

In the context of nuclear forensics and comparing the δ^{234}U and δ^{238}U of a UOC of known provenance to an unknown seized sample, there is potential for UOC processing to modify the uranium isotope compositions and consequently mislead an investigation. For example, where a UOC of known provenance and an unknown seized UOC are sourced from the same mine but processed at different points in time (i.e. as different batches), inconsistent isotopic compositions caused by batch to batch variance may lead an analyst to incorrectly conclude the two samples are different. Although the reproducibility of these observed changes in isotopic composition have not been studied here, when considering the variability of δ^{234}U and δ^{238}U in nature, it is conceivable that a dilute sulphuric acid leach may yield a variable U isotope signature. We recommend future studies in this area to evaluate the reproducibility of U isotope changes caused during these chemical processes that are typical of the nuclear fuel cycle.

Localised isotopic heterogeneity and changes to the U isotope signature caused by a weak sulphuric acid leach have the potential to mislead a nuclear forensics investigation where δ^{234}U and δ^{238}U are relied upon. The circumstances discussed above highlight the requirement for a subject matter expert (SME) to review these signature data prior to applying the subsequent statistical tools associated with the comparative signature approach. We recommend the respective SME is aware of the potential for perturbation of δ^{234}U and δ^{238}U as highlighted in this paper. While there is some potential for these signatures to misinform, it is important to recognise that the analytical techniques used in this study quote more precise values (±0.04‰ for δ^{238}U and ± 0.4 ‰ for δ^{234}U) relative to those given in the nuclear forensics investigation reported in Keegan et al. (2016) (relative uncertainty k=3, ^{235}U/^{238}U = 0.2 %, ^{234}U/^{238}U = 0.6 %). At these lower precisions it is not possible to discriminate between the differences in isotopic composition as discussed in this paper. While this may trivialise the issue of changes to the U isotopic composition during processing, less precise data inevitably reduce the discriminatory power of these signatures.

5 Conclusions

In this study, $\delta^{238}U$ and $\delta^{234}U$ have been determined for vein type uranium ore deposits collected mainly from mines in central Portugal and SW England. The data presented are in agreement with mean $\delta^{238}U$ and $\delta^{234}U$ values for other vein type uranium deposits reported elsewhere in the literature. Notably, the range in $\delta^{234}U$ measured here is significantly larger than current available literature data for U vein type deposits, with both negative and positive values with respect to secular equilibrium.

There is overlap between $\delta^{238}U$ and $\delta^{234}U$ values obtained for samples from SW England and Portugal. However, there is a tendency for the Portuguese $\delta^{234}U$ to be higher relative to the English samples and vice versa for $\delta^{238}U$. It was not possible to use these signatures to distinguish between different regions of the same country or different mines of the same country. When comparing reduced U versus oxidised U mineral phases, we observe a distribution with lower average $\delta^{238}U$ values for oxidised U samples, which follows the nuclear field shift theory for U isotope fractionation observed elsewhere. Although it is expected that U isotopic heterogeneity within the sample will also play a role in this observation. The majority of the $\delta^{234}U$ values are close to secular equilibrium, but some of the U^{6+} (uranyl) minerals exhibit considerably more variable $\delta^{234}U$, suggesting within mine mobility of U within the last two million years.

Variable $\delta^{238}U$ and $\delta^{234}U$ are observed for samples collected from within the same mine and vein at the Carbis Bay and Kingswood mines. Leaching several of these samples in dilute sulphuric acid for 24 hours caused both $^{235}U/^{238}U$ and $^{234}U/^{238}U$ to change unpredictably. The dissimilar patterns of $\delta^{238}U$ and $\delta^{234}U$ indicate these two signatures are decoupled and rely on different mechanisms. These findings suggest UOCs produced from ore extracted from the same mine, via the same procedures, can yield variable $\delta^{238}U$ and $\delta^{234}U$.

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