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Rhenium Isotope Reconnaissance of Uranium Ore Concentrates

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ABSTRACT

Exploration of natural isotopic variations of the element rhenium (Re) is in its infancy, with initial studies revealing isotopic fractionation in a variety of geological materials. Here, we investigate Re isotope variation as a new geochemical tool, given its redox-sensitive properties and affinity for organic matter and sulfides. In this work, Re abundance and isotope ratio data were collected from uranium ore concentrates (UOCs) across a variety of depositional ages, locations, geologic settings, and deposit types. Ore types from which the UOC were derived include sandstone, unconformity, and quartz-pebble (QP) conglomerate. To isolate Re from the U-rich matrix of UOCs, a new purification method utilizing DGA ion exchange resin was developed. We found that UOCs exhibit a wide range of Re isotope ratios, with sandstone ore-derived UOCs having the isotopically lightest values, QP conglomerate ore-derived UOCs having the heaviest, and unconformity ore-derived UOCs in between (with some overlap with sandstone UOCs). The Re isotope ratio range observed in UOCs extends previously reported values by more than a factor of two. Industrial processing (e.g., incomplete recovery of Re from ore, contamination, fractionation during processing) may play a role in the isotopic variability in the UOCs. However, systematic differences between ore types suggest that the depositional setting is a significant factor. For nuclear forensic investigations, Re isotopic compositions combined with data from other isotopic systems provide geochemical signatures that can aid in provenance assessment of UOCs. Regardless of the specific causes for the wide range of Re isotope ratios in UOCs, these initial data indicate Re is a promising tool for nuclear forensic investigations on samples from early in the nuclear fuel cycle.

1. Introduction

Rhenium (Re) is a siderophile and chalcophile transition metal sensitive to environmental oxygen (i.e., redox sensitive) with important scientific and industrial applications (Brenen, 2018; Werner et al., 2023). Rhenium is one of the least abundant naturally occurring elements at Earth's surface with a typical upper continental crust concentration of ~200 pg / g (Rudnick and Gao, 2003). Its abundance is elevated in certain rocks, such as organic rich mudrocks (ORM; commonly but imprecisely referred to as "black shales"), and in molybdenites, due to its redox sensitive properties (e.g., Koide et al., 1986; McCandless et al., 1993).

Rhenium has two isotopes, ^{185}Re and ^{187}Re, with average relative natural abundances of 37.4 % and 62.6 %, respectively. The isotope ^{185}Re is stable, whereas ^{187}Re is radioactive with a half-life of approximately 41.6 billion years (Smoliar et al., 1996; Selby et al., 2007), which is long enough to allow it to be treated as stable for purposes as a geochemical tracer. The β^- decay of ^{187}Re into ^{187}Os is the basis of the widely used Re-Os dating technique.

Recent studies of natural Re isotope fractionation explored the potential use of the Re isotopic system to infer past paleoenvironmental conditions (Miller et al., 2015), trace the oxidative weathering flux of petrogenic organic carbon through time (Dellinger et al., 2020, 2021), and understand early Solar System processes (Liu et al., 2017). The isotopic variability found to date spans 1.06 ‰ (Fig. 1), from −0.97 ‰ to 0.09 ‰ (Miller et al., 2015; Liu et al., 2017; Dickson et al., 2020; Dellinger et al., 2020, 2021; Wang et al., 2024). The lightest value is from a heavily weathered ORMs (Miller et al., 2015) and the heaviest value is from an iron meteorite (Liu et al., 2017).

Here, we examine Re isotopes in uranium ore concentrates (UOC; also known as yellowcake). UOC are friable solids containing ~60–80 wt. % U which are produced during industrial processing of natural U-

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rich geologic materials. UOCs are globally regulated nuclear materials that can be obtained on the open market, and so geochemical signatures are often used to trace the source of the UOC when they are found outside regulatory control (e.g., Kristo et al., 2016). During milling of ore material to produce UOCs, the U-rich ore is crushed and put through successive processes of extraction and purification of U, followed by precipitation as a solid. The exact methods for U extraction vary based on the chemical composition of the ore material, but it is possible to retain the geochemical signatures of the ore material during production of UOC – including isotope abundances. Rhenium abundances in UOC are variable and can be orders of magnitude greater than in upper continental crust (e.g., Denton et al., 2022). However, Re isotopic variations in UOCs have yet to be explored. Exploration of other elemental abundances and isotope ratios (e.g., U, Mo, Sm, Nd, Pb) in UOCs have provided information about the natural behavior of these elements, and are useful for nuclear forensic investigations (e.g., Varga et al., 2009, 2017, 2023; Brennecka et al., 2011; Rolison et al., 2019; Migeon et al., 2020; Shollenberger et al., 2021; Devlin McLoughlin et al., 2023).

To provide tighter constraints and higher confidence in provenance assessment of an interdicted UOC, it is beneficial to have data from multiple geochemical signatures, which motivates the exploration of Re isotopes in UOC.

Because nuclear forensic investigations often aim to tie UOC back to the original ore deposit from which it was mined, it is important to examine how Re isotopes might vary among different UOCs from different depositional environments. Uranium ore can be hosted in multiple deposit types, which often have distinct formation mechanisms. UOC ore types are defined by the International Atomic Energy Association (IAEA).

“Sandstone-type” deposits form in low-temperature settings from continental fluvial, lacustrine, or shallow-marine sedimentary environments. Uranium enrichments occur when low-temperature oxidized

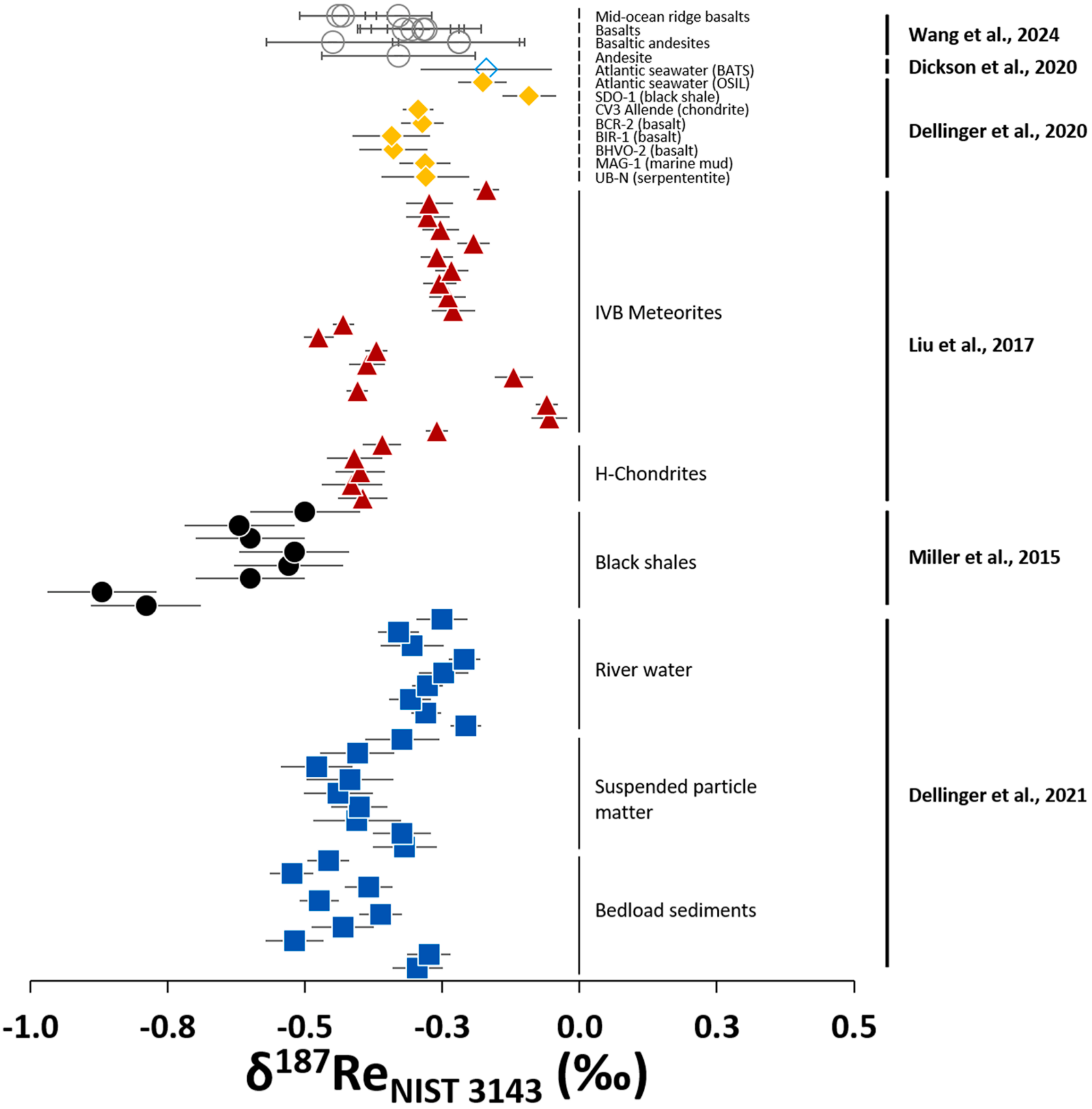

Fig. 1. Previously Published Re Isotope Ratio Data. Rhenium isotope ratio data are presented as δ^{187}Re (‰; defined in Section 2.3). Figure shows the δ^{187}Re data in the peer-reviewed literature, presented using NIST 3143 as the normalizing standard. Data are from Miller et al. (2015), Liu et al. (2017), Dickson et al. (2020), Dellinger et al. (2020, 2021), and Wang et al. (2024). Error bars are from the source publications, with Miller et al. (2015), Dellinger et al. (2020, 2021), and Dickson et al. (2020) representing ±2SD, and Liu et al. (2017) and Wang et al. (2024) representing +2SE. One Fe-meteorite sample from Liu et al. (2017) with a very light δ^{187}Re value (−1.84 ± 0.03 ‰ 2SE), is excluded because a replicate analysis of the same sample with a value of -0.12 ± 0.03 ‰ 2SE indicates the very light isotopic composition was not reproducible. BATS = Bermuda Atlantic Time-series Study. OSIL = Ocean Scientific International Ltd.

fluids (carrying soluble U^{VI}) interact with a reducing agent and precipitate U as U^{IV} (IAEA, 1985). While sandstone is not a major host of authigenic Re, ORMs—a rock type that can have high abundances of Re—is commonly interbedded in sandstone-type deposits. Therefore, the range of Re abundance in UOCs created from sandstone ore is likely to vary based on how much ORM material is included during the mining process.

"Unconformity-type" deposits form in high-temperature settings associated with metamorphic processes, and include some of the largest and most abundant U deposits globally (IAEA, 2020). These deposits form from sandstone ore that was overlying basement rocks (often Archean to Paleoproterozoic aged) and experienced fluid alteration (IAEA, 2020). Similar to sandstone-type deposits, this category includes U deposited via reduction of soluble U^{VI} to insoluble U^{IV}. The U ores often take the form of veins, breccias, and replacements. Since mining operations target the veins and breccias, Re abundances are expected to be low as these materials are not a major host for Re.

"Quartz-Pebble (QP) conglomerates" are ancient U deposits formed during the Archean Eon (IAEA, 2020). There is ongoing debate as to whether QP conglomerates are of detrital or hydrothermal origin (see Burron et al., 2018 and references therein). Regardless of the specific emplacement mechanism, QP conglomerates formed prior to the emergence of a widely oxygenated planet, when the absence of O_2 in the atmosphere and ocean inhibited the release and mobility of Re. Therefore, the abundance of Re in QP conglomerate deposits is expected to be low.

Here, we present the first δ^{187}Re data from UOC samples. Twelve UOC samples were analyzed that were derived from U-rich ore material, including from sandstone, unconformity, and QP conglomerate ores.

2. Samples and Methods

We targeted samples from Lawrence Livermore National Laboratory (LLNL) previously investigated for other isotopic systems. This focus allows for direct comparison of different isotopic signatures and elemental abundances. The countries of origin and deposit types of these samples were previously reported in Brennecka et al. (2010), Krajkó et al. (2014), Reading et al. (2016), and Shollenberger et al. (2021).

2.1. Sample Preparation

2.1.1. Digesting UOC samples

We used high-purity Seastar Baseline® concentrated nitric acid (HNO_3) and hydrochloric acid (HCl) throughout the sample dissolution, sample preparation, and processing procedures. Milli-Q® water (18.2 MΩ-cm) was used for all dilutions. All sample processing was completed at LLNL in a trace metal clean laboratory. All digestions and dry downs were done in acid cleaned Savillex® Teflon beakers.

Powdered UOC samples (sample weights ranged from 0.13 – 2.49 g) were weighed and placed in Teflon beakers with 4 molar (M) HNO_3 on a hotplate at 140 °C for 72 h. While this process fully dissolved many of the samples, in some cases there was residual undissolved material. Undigested samples were dried down and reconstituted in ~4 ml of concentrated HCl, capped, and heated at 140 °C overnight. This digestion step was followed by drying down, after which 5 ml of aqua regia was added to the samples which were then capped again and heated overnight at 140 °C.

2.1.2. Purifying Re with Column Chromatography

Rhenium was purified from UOC samples using a N,N,N'N' tetraoctyl-1,5-diglycolamide (hereafter DGA) resin column chromatography protocol developed as part of this study to optimize the removal of U which makes up a majority of the matrix. In preparation for column chromatography, all digested samples were centrifuged at 3000 RPM for 5 min in 15 ml centrifuge tubes in 10 ml 0.5 M HCl. Centrifugation was done to remove any particles, visible or not, from the dissolved samples. The supernatant was decanted into clean Teflon beakers. These decanted samples were then loaded onto 2 ml resin cartridges packed with DGA resin (Eichrom) with a particle size of 50 – 100 μm and a resin length and diameter of ~2.8 cm and ~0.8 cm, respectively. The column chemistry was completed in a vacuum box with a flow rate of ~1.5 ml/min to isolate Re (Table 1). This column chemistry protocol was designed based on elemental partition coefficients for DGA resin (Pourmand and Dauphas, 2010).

Prior to being loaded with samples, the DGA resin cartridges were cleaned using the eluting acids and then conditioned with 0.5 M HCl. The samples were loaded in 10 ml 0.5 M HCl. The matrix removal steps (Table 1) were loaded in 5 ml increments which were allowed to pass through the column completely before the next volume was added. Rhenium was eluted into clean Teflon beakers with 12 ml of 10 M HNO_3 in increments of 2 ml, 4 ml, 4 ml, and 2 ml. The entire procedure, starting from cleaning the resin, was repeated 2–3 times for each sample. This was done to ensure complete removal of native tungsten (W) from the samples, which was determined by analyzing an aliquot of each sample prior to isotopic measurement. Rigorous removal of W was needed because a W standard is added to the samples before isotopic analysis as a way of monitoring and correcting for mass bias during analysis (discussed further in the SI).

The chemical separation process successfully extracted the majority of Re from the samples with high yields. The UOC standard CUP-2 was included in this study and has a reference Re abundance of 24 ± 8 (2SD) ng/g (Denton et al., 2022). We measured a CUP-2 Re abundance, post-chemistry, of 19 ± 2 ng/g (2SD). Furthermore, 100 ng of the Re standard NIST 989 was put through the column chemistry procedure and a recovery of 100 ± 6 % was calculated between the post- and pre-chemistry samples.

To remove any residual organic material from the resin that might be present in the Re elution solutions, the samples were fluxed and dried down in ~200 μl of aqua regia in Savillex® beakers at 140–150 °C. This procedure was repeated until the samples were visibly colorless when dissolved in ~1 – 2 ml of 0.32 M nitric acid and the solution did not stick to the walls of the Teflon when rotated, which we took as an indication of near complete removal of organic material from the samples. A process blank was collected in parallel with the samples, following the same procedures. We found a total blank contribution of 195 pg Re ($n = 1$), less than 1 % of the Re in each sample, which we considered negligible.

2.2. Elemental Concentration Analyses

Rhenium abundances were measured with a Thermo Scientific iCAP-Q at Arizona State University. An aliquot representing ~1 % of the post-column chromatography Re elution solution was taken from each sample and diluted with 0.32 M HNO_3. Due to the matrix effects from U in unpurified UOCs, the Re concentrations reported here were determined from aliquots after the first round of column chemistry, rather than the unprocessed dissolved samples.

All samples were analyzed in the same analytical session, using a multi-element calibration standard. An internal standard containing *Sc*, Ge, Y, In, and Bi was introduced to the instrument in parallel with all

Table 1
Column Chemistry Protocol to Purify Re from UOCs using DGA resin.

Description	Volume (ml)	Acid Molarity	Acid Type
Wash Resin	5	10	HNO_3
	5	0.5	HNO_3
	5	0.1	HNO_3
Condition Resin	10	0.5	HCl
Load Sample	10	0.5	HCl
Matrix Removal	15	0.5	HCl
	10	0.5	HNO_3
	5	0.1	HNO_3
Elute Re	12	10	HNO_3

samples and standards to correct for signal drift. A standard containing all the elements in the calibration standards was analyzed every five samples to assess accuracy and precision throughout the analytical session. The relative standard deviation of each analyte in the standard was typically less than 2 %, and the uncertainty associated with each abundance measurement is ± 10 %.

2.3. Isotope Ratio Analyses

Rhenium isotope ratios were measured on a Thermo Scientific Neptune Plus multi collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at LLNL in low resolution mode. Tungsten, which has a similar mass and ionization efficiency to Re, was used to correct for internal mass bias during each analytical session, as has been demonstrated in the literature (Miller et al., 2015; Liu et al., 2017; Dickson et al., 2020; Dellinger et al., 2020, 2021). After all samples were determined to have near-blank intensities at the masses of the W isotopes, a W standard was added to each sample. Samples were measured on the Neptune as 20 ng/g Re and 35 ng/g W in 0.32 M HNO_3 which provides the required precision for meaningful Re isotope ratio data. The samples were introduced to the plasma with an Apex 2 IR desolvating nebulizer via aspiration at a flow rate of ~50 µl min^{-1}. Each isotope was monitored on a Faraday detector with 10^{-11} Ω resistors. Blanks were analyzed intermittently throughout the analytical sequence and were less than 1 % of the signal on ^{187}Re and ^{186}W. The ^{187}Re ion beam intensity of each sample was confirmed to match the intensity of the ^{187}Re ion beam for the bracketing standard (NIST 3140) by ± 10 %.

The isotopic compositions of Re are reported in delta (δ) notation shown in Eq. (1).

$$\delta^{187}\mathrm{Re}(‰) = \left[\left({}^{187}\mathrm{Re}/{}^{185}\mathrm{Re}\right)_{\mathrm{sample}}\Big/\left({}^{187}\mathrm{Re}/{}^{185}\mathrm{Re}\right)_{\mathrm{NIST\ 3143}} - 1\right] \times 1000 \tag{1}$$

The δ^{187}Re data are reported as an average of multiple runs, except for one sample (Enusa) which was run only once due to limitations in the amount of Re in the sample. Uncertainties are listed as ±2SD of replicate analyses of samples when $n \geq 3$, or the uncertainty of replicate standard analyses of NIST 989 (± 0.05 ‰ 2SD, $n = 22$), whichever is larger.

Because W begins to precipitate out of solution in dilute nitric acid with no HF within weeks to months, all samples and standards in this study were analyzed within hours to days after the addition of W.

2.3.1. Accuracy and Precision of Re Isotope Measurements

In addition to using W during Re isotopic measurements to correct for mass bias, standard-sample-standard bracketing was also used throughout all analytical sessions. The accuracy and precision of the Re isotope measurements was assessed by analyzing the Re standard NIST 989 compared to the Re standard NIST 3143 throughout data collection process. These materials were introduced to the MC-ICP-MS in 0.32 M HNO_3, the same acid and molarity as all samples. The repeated analysis of NIST 989 yielded $\delta^{187}\mathrm{Re} = -0.28 \pm 0.05$ ‰ (2SD, $n = 22$) (table S1). This value agrees with previous studies (Miller et al., 2015; Liu et al., 2017; Dickson et al., 2020; Dellinger et al., 2020, 2021). As NIST 989 is no longer in production, the Re standard NIST 3143 was used for the δ=0 value, as in Dickson et al. (2020).

As a quality control test to check for mass fractionation during the chromatography, the Re standard SRM 989 was processed through the chemistry protocol and its isotopic composition measured. The measured isotopic composition agrees with that of the unprocessed standard within uncertainty (Table S1). Further quality control tests including analysis of replicate digestions and tests examining the effect of a high U matrix on Re isotope ratio measurements can be found in the supplemental material.

3. Results

3.1. UOC Re Geochemical Data

Twenty-two UOC samples with unknown Re abundances were processed at LLNL. Ten of the 22 UOC samples had too little Re (< 5 ppb *Re*) for isotope ratio measurements. Of the twelve UOC samples that had sufficient Re for isotope ratio measurements, we found a δ^{187}Re range of −0.99 to 1.33 ‰ (Table 2, Fig. 2). This range in δ^{187}Re variations are significantly greater than the minimum uncertainty associated with δ^{187}Re measurements of 0.05 ‰ (2SD, $n = 22$) determined by analyses of standards.

Of the measured UOCs, eight were derived from sandstone deposits. Their δ^{187}Re ranged from −0.99 to 0.62 ‰ with an average of −0.41 ‰. The abundance of Re ranged from 37 to 1795 ng/g. Three UOC samples derived from unconformity deposits were analyzed and the δ^{187}Re ranged from −0.31 to +0.37 ‰. The abundance of Re ranged from 14 to 36 ng/g. The lone QP conglomerate deposit had a Re abundance of 19 ng/g and a δ^{187}Re of 1.24 ‰ ± 0.09 ‰ (2SD; $n = 3$).

4. Discussion

The UOC samples from this study were created by milling U-rich ore material. The milling procedure consists of chemical leaching, solvent extraction, ion exchange separation techniques, and evaporation. However, the exact procedures that these samples underwent are unknown. Therefore, there are two possibilities to explain the δ^{187}Re values in the UOC samples: 1) The δ^{187}Re data from UOCs represent the bulk isotopic composition of the ore material it is produced from, or 2) δ^{187}Re data of UOCs is offset due to fractionation during processing and/or contamination. These possibilities are discussed in detail below.

4.1. Re Abundance and δ^{187}Re of the UOC Samples

There is high variability in the abundance of Re in the UOC samples, ranging from < 10 ng/g to ~1800 ng/g (Fig. 3). For context, the average Re abundance of Phanerozoic ORMs is ~155 ng/g (Sheen et al., 2018), and the average Solar System abundance (CI chondrites) is ~37 ng/g (Anders and Grevesse, 1989; Lodders, 2003). While some of the Re concentration variation in UOCs could be caused by the processing of the ore, we observe a distinct difference in the range of Re abundances between UOCs derived from sandstone-type ores (37–1795 ng/g; $n = 8$), and UOCs derived from unconformity-type ores (<10 – 36 ng/g; $n = 3$), or the QP conglomerate ore (19 ng/g; $n = 1$). Even though sandstone is not a major host of Re, the large range of Re concentrations can be explained naturally if there are varying degrees of incorporation of ORMs with the mined sandstone ore material. This is because Re (and U) in low temperature aqueous settings under reducing conditions is readily sequestered with organic matter and/or sulfides (e.g., Colodner et al., 1993, 1995; Helz and Dolor, 2012; Morford et al., 2012; Helz, 2022). Thus, interbedding of ORMs in sandstone-type ores could lead to UOCs with high Re abundances. We find no correlation between Re abundance and δ^{187}Re ($r^2 = 0.0877$ across all 12 samples; Fig. 3), which indicates that the source(s) of Re in the high and low abundance samples have a wide range of Re isotopic values that have some overlap.

If ORM incorporation is the reason for the very high Re abundances of some sandstone ore-derived UOCs, then the Re isotopic composition of these UOCs could reflect that of the waters beneath which the sedimentary precursors of these ORMs were deposited. If this is the case and there is no isotopic fraction imparted during UOC production, it would imply that the isotope compositions of ORM exhibit a wide range of fractionation.

Alternatively, if the high Re content of some sandstone ore-derived UOCs is not caused by inclusion of ORMs, then Re contamination from a reagent used during UOC processing could be the cause. In this case, the Re-containing reagent would dominate the isotopic composition of

Table 2

UOC Re Geochemical Data. δ^{187}Re, [Re], geologic information, and sample identifiers for UOC samples. NIST 3143 is used as δ=0. *n* indicates the number of replicate analytical measurements. Errors for δ^{187}Re data represent the 2SD of replicate analyses, or the 2SD of replicate standard analyses, whichever is larger. IAEA = International Atomic Energy Agency.

Category	Deposit Type	Country and Identifier	Re (ng/g)	δ^{187}Re (‰)	2SD	*n*	Basin / Region	Approx. Age	Age/Region Source
Low-temperature redox	Sandstone	Niger – Somair	1795	0.18	0.07	3			
	Sandstone	USA - Chevron Hill	81	0.57	0.05	4			
	Sandstone	USA - Everest Yellow	37	−0.47	0.05	4			
	Sandstone	USA – Irigary	1263	−0.72	0.05	4	Wyoming (WY)		IAEA database
	Sandstone	USA – Pathfinder	86	−0.73	0.05	4	Wind River, WY	22 Ma	Dooley et al., 1974
	Sandstone	USA – Petrotomic	775	−0.94	0.05	4			
	Sandstone	USA - Shirley Basin	532	−0.67	0.06	4	Wind River, WY	22 Ma	Dooley et al., 1974
	Sandstone	USA - Union Carbide	924	−0.49	0.08	16			
High-temperature redox	Unconformity	Australia – Rum Jungle	36	−0.23	0.08	4	N. Territory	1627–232 Ma	Von Pechmann, 1986
	Unconformity	Canada – Key Lakes	30	0.29	0.08	5			
	Unconformity	Spain – Enusa	14	0.13	0.05	1			
Non-redox	QP Conglomerate	Canada - Blind River (CUP-2 standard)	19	1.24	0.09	3	Elliot Lake	2.45–2.2 Ga	Bennett et al., 1991

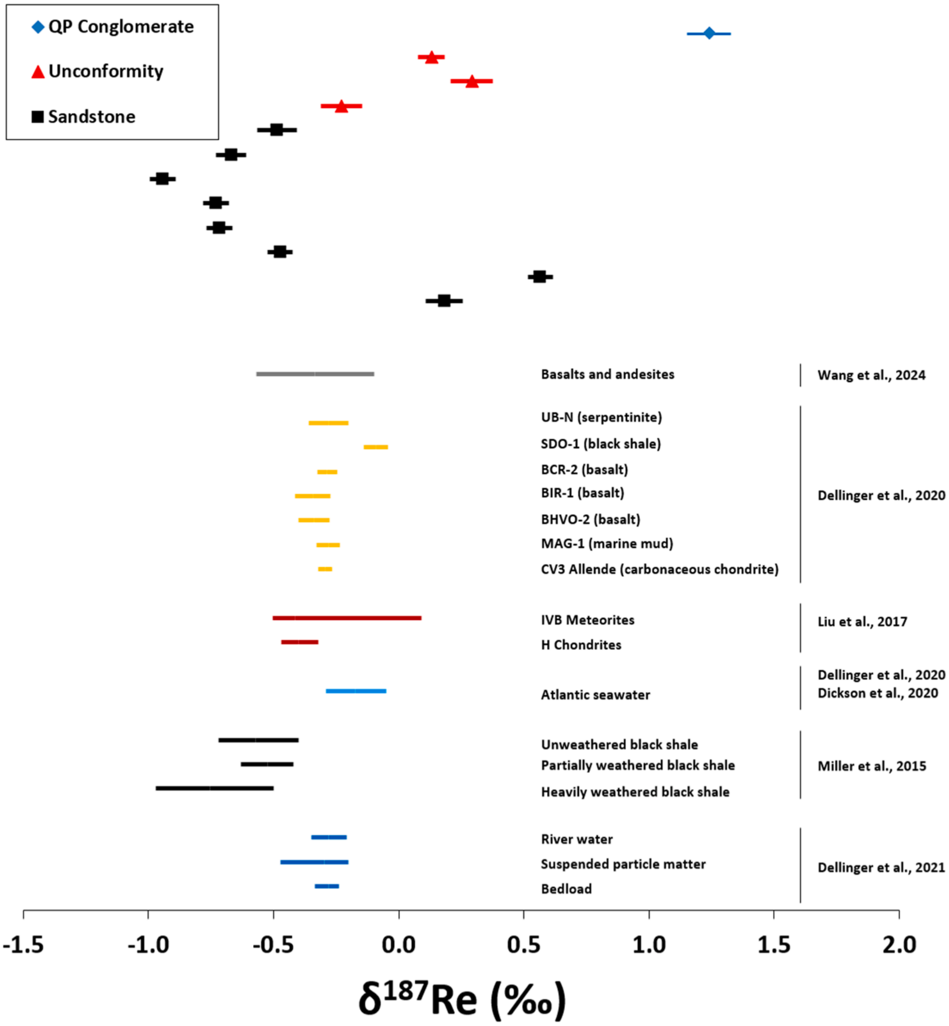

Fig. 2. UOC Data with Published Re Isotope Ratio Data: Uranium ore concentrate δ^{187}Re data grouped by ore type: sandstone (black square), unconformity (red triangle), and quartz-pebble (QP) conglomerate (blue diamond) with published δ^{187}Re data (using NIST 3143 as the normalizing standard; Miller et al., 2015; Liu et al., 2017; Dickson et al., 2020; Dellinger et al., 2020, 2021; Wang et al., 2024). Error bars for UOC data represent ±2SD of replicate analyses, or ±2SD of replicate standard analyses, whichever is larger.

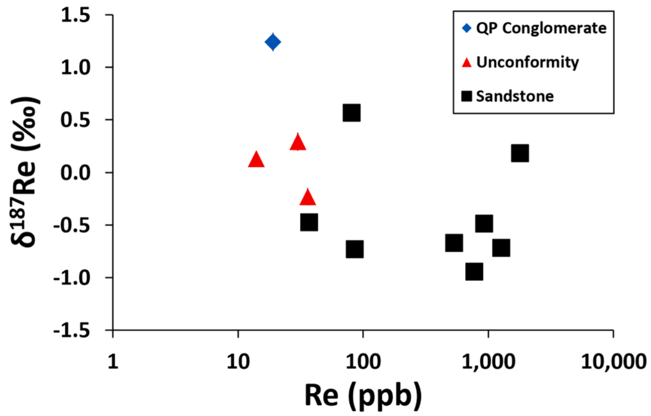

Fig. 3. UOC Re Isotopes vs. Re Abundance. Rhenium isotopic composition (given as δ^{187}Re) compared to Re abundance (log scale). The figure highlights the lack of correlation between Re abundance and isotopic composition for the ore types and the large range in [Re] of UOC in the samples. The r^2 value calculated from all UOC data is 0.0877 which indicates no correlation between δ^{187}Re and Re abundances. The error bars of the δ^{187}Re data represent the 2SD of replicate analyses, or the 2SD of replicate standard analyses, whichever is larger. In most cases, the symbol is larger than the error bar.

the samples and could be used to narrow down the processing location of a sample if there is prior knowledge of the isotopic composition of such reagent. However, if this is the case, it would mean there is not a common Re isotopic composition for the hypothetical contaminant as there is a wide range of Re isotopic values in the high Re abundance samples. This could mean that the isotopic composition of contaminants is variable at different processing locations. Additionally, a combination of natural Re and Re contamination is also possible.

4.1.1. *Sandstone Ore δ^{187}Re Data*

The δ^{187}Re values in sandstone ore-derived UOCs have the widest range of Re concentrations and isotopic compositions of all ore types, with a δ^{187}Re range from −0.99 ‰ to +0.62 ‰. Sandstones are derived from weathered continental material. So far, the Re isotopic composition of granitic material is yet to been analyzed, but Re abundances in granitic material are low (~200 pg/g; Rudnick and Gao, 2003). The silicate rocks analyzed in Wang et al. (2024) have similar δ^{187}Re values of ~ −0.3 ‰ and could possibly be similar to the isotopic compositions of granitic material.

Three of the UOC samples with mine location information – Irigary, Pathfinder, and Shirley Basin – were derived from Wyoming, USA (Dooley et al., 1974; IAEA Database). The δ^{187}Re values are indistinguishable within uncertainty at ~0.70 ‰, however, the Re abundances of Irigary, Pathfinder, and Shirley Basin are 1263 ppb, 86 ppb, and 532 ppb, respectively. The consistent Re isotope ratio despite wildly different Re concentrations for these samples may indicate that the Re

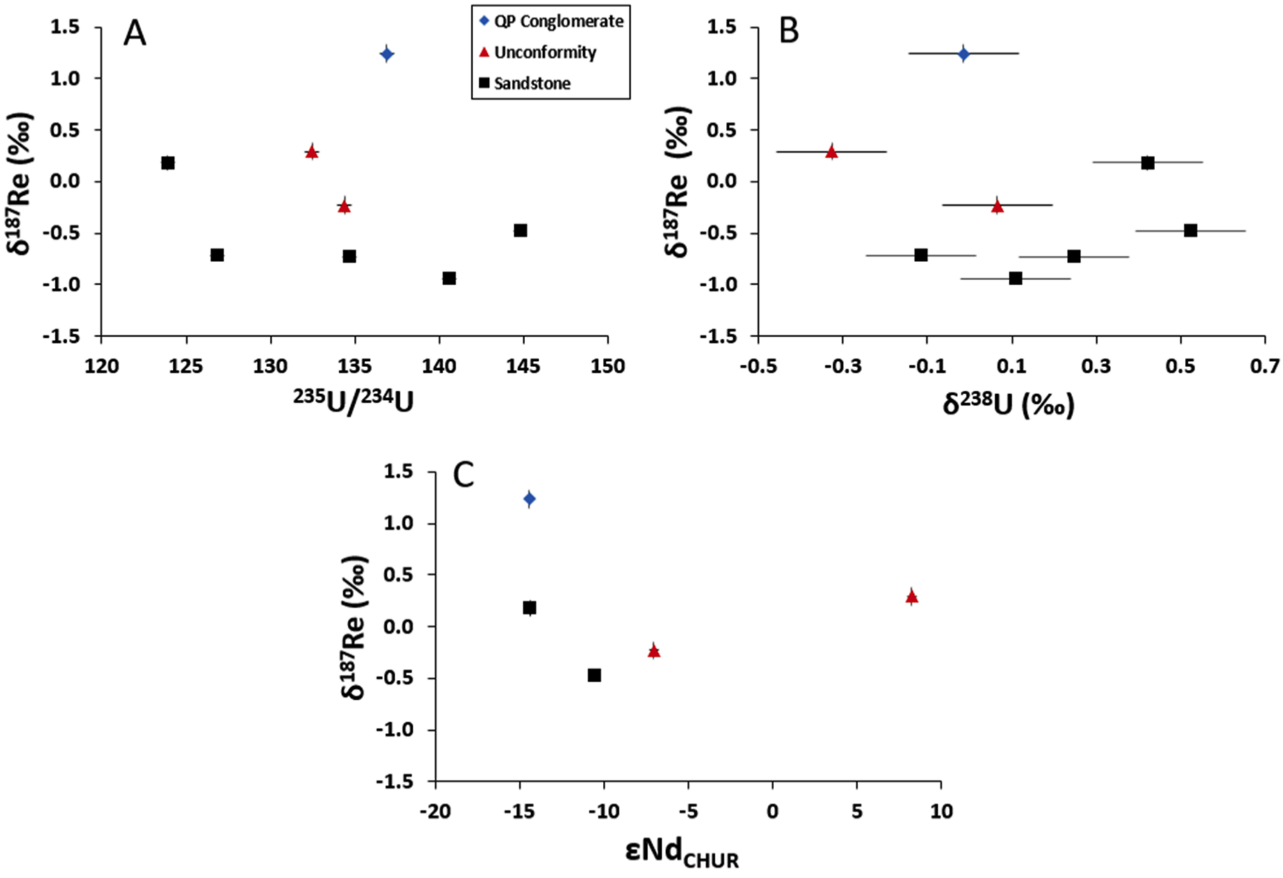

Fig. 4. UOC Re Isotopes Compared to U and Nd Isotopes: δ^{187}Re (‰) data compared to U isotope (panels A and B) and Nd isotopes (panel C). These plots highlight the unique combinations of Re isotope ratios vs. U and Nd isotope ratios, providing a potentially unique geochemical signature for each sample that can be helpful in identification of the location a UOC sample was processed from. Not all UOC samples in this study had comparable U isotope and Nd isotope data. The εNd values represent parts per 10,000 deviations of a sample ^{143}Nd/^{144}Nd relative to the Chondritic Uniform Reservoir (CHUR). U isotope data are from Brennecka et al. (2010). Nd isotope data are from Krajkó et al. (2014) and Devlin McLoughlin et al. (2023). Uncertainties in δ^{187}Re represent the 2SD of replicate analyses, or the 2SD of replicate standard analyses, whichever is larger. In most cases, the symbols are larger than the error bars. U and Nd isotope error bars represent the error on standards from the papers they were collected from.

isotopic composition from ore material in this area is similar. Alternatively, the Re isotopic compositions may be dominated by Re contamination from a reagent used during the milling process in that region. In either case, the consistency of the Re isotopic compositions for samples from the same region may either provide a signature of the geology of that region, or a signature of the processing technique using a specific Re-containing reagent. Either of these outcomes would be important in a nuclear forensic investigation.

4.1.2. Unconformity Ore δ^{187}Re Data

The δ^{187}Re values of unconformity-type ores ranged from −0.31 to +0.37 ‰. The average δ^{187}Re value for unconformity ore fell between the average for sandstone-type and QP conglomerate ore-derived UOCs. There is some overlap with UOCs derived from sandstone-type ores (Fig. 2). The Re abundance of basement rocks is estimated to be very low (< 200 ppt *Re*) based on Re geochemical abundances in continental material. Therefore, the Re in these UOCs is likely primarily derived from the overlying sandstone material which may also include organic-rich material, similar to UOCs derived from sandstone-type ores. However, because these deposits likely formed before the Phanerozoic eon, it is possible that the Re abundance in organic rich material would be lower than in Phanerozoic derived organic rich material as there was likely less Re in seawater due to lower delivery of Re to the ocean via oxidative weathering of continental material (Sheen et al., 2018). This would lead to unconformity ore-derived UOCs with lower Re abundances on average compared to Phanerozoic sandstone ore-derived UOCs.

Unconformity deposits form from ore that experienced fluid alteration (IAEA, 2020). If the fluids were oxygenated, it is possible that Re could have been remobilized from a solid phase by oxidation (e.g., Morford et al., 2005, 2009, 2012) via a change in redox state to $\mathrm{Re}^{\mathrm{VII}}$ forming the soluble anion perrhenate. The oxidation of Re would likely introduce mass-dependent fractionation between the mobilized Re and the retained Re in the ore if there was incomplete oxidation of the ore material. This would alter the δ^{187}Re value of the ore material which could be a natural geologic explanation for the large range in Re isotope ratios in these UOCs. Additionally, precipitation of Re from a fluid phase after remobilization could also lead to isotopic fractionation in this setting. It is important to note that since unconformity type-ores form in high temperature settings, isotopic fractionation is expected to be smaller in magnitude than in low temperature settings (Urey, 1947).

4.1.3. Quartz-Pebble conglomerate Ore δ^{187}Re Data

QP conglomerate UOCs are derived from materials that formed in the Archean prior to the emergence of a persistently oxygenated atmosphere and ocean. Thus, the ore material possibly has not been influenced by redox processes related to the presence of O_2. The sole QP conglomerate ore-derived UOC sample exhibits a δ^{187}Re of 1.24 ± 0.09 2SD.

The formation mechanics for QP conglomerates are uncertain, with debate about if they are hydrothermal or detrital in origin (e.g., Burron et al., 2018 and references therein). If QP conglomerates have a detrital origin as Burron et al. (2018) suggest, then the uraninite and other material present in the QP conglomerates may represent eroded material from rocks and minerals. Alternatively, if the QP conglomerates have a hydrothermal origin, the heavy δ^{187}Re value may indicate that high temperature hydrothermal settings can lead to heavy isotopic compositions.

4.2. Possible Isotopic Fractionation Pathways During UOC Production

The milling process involves many steps, many of which can induce isotope fractionation. These primarily include leaching, evaporation, solvent extraction, ion exchange, and precipitation. There has not been a comparison of the Re isotopic composition of ore material and the paired UOC to examine if there is fractionation introduced during UOC processing. However, molybdenum (Mo) isotope geochemical behavior has been examined between mining material and the paired UOC that it was produced into (Migeon et al., 2018, 2020; Rolison et al., 2019). These data can be used to make educated assumptions about Re behavior during the milling process because Mo is an element with similar geochemical behavior to Re (e.g., Crusius et al., 1996). The milling process has been found to lead to Mo isotope fractionation in both positive (leaching, evaporation) and negative (solvent extraction, ion exchange, precipitation) directions, with the magnitude of fractionation related to the recovery of Mo and the type of processes utilized during purification (Migeon et al., 2018, 2020). The range of Mo fractionation in UOC extends to more negative isotope values than has been found in natural systems, by ~ 1 ‰ (see Kendall et al., 2017). Additionally, Rolison et al. (2019) found up to + 0.75 ‰ fractionation in Mo isotopes from UOC and U-ore, which could plausibly be explained by adsorption of the lighter Mo isotopes to Fe-Mn oxides which are created as secondary minerals during milling (Migeon et al., 2018). However, adsorption to Fe-Mn oxides is likely not a fractionation mechanism for Re, as Re does not significantly adsorb to Fe-Mn oxides (Yamashita et al., 2007). Therefore, this process would likely not influence the isotopic composition of Re in UOCs.

A UOC processing effect that could impact Re chemistry is if Re was incompletely removed from ore material, or incompletely recovered during ion exchange purification procedures. Studies of Re purification via column chromatography using AG 1-X8 (100–200 mesh) resin show that during Re recovery, the initial isotopic composition of Re that is collected is isotopically heavy, with the first 30 % of Re being isotopically heavy by ~0.35 ‰ (Miller et al., 2009). This behavior is consistent with what has been reported from studies of other isotope systems on different resins (e.g., Ca: Russell et al., 1978; Fe: Anbar et al. 2000; Roe et al., 2003; W: Irisawa and Hirata, 2006). If industrial purification processes behave similarly to laboratory processes, it is likely that fractionation introduced from incomplete recovery of Re would lead to heavier Re isotope ratios in the soluble phase, leaving light isotopes on the ion exchange resin. Varga et al. (2017) examined elemental abundances in UOCs and paired QP conglomerate ore material and found low recovery of Re during the processing of the QP conglomerate ore. It is unknown if the QP conglomerate UOC in this study (CUP-2) underwent the same processing methods as the samples from Varga et al. (2017), but it is interesting that CUP-2 has the heaviest δ^{187}Re (1.24 ± 0.09 ‰ 2SD) of any sample measured so far. However, the maximum fractionation from incomplete recovery of Re during column chromatography found so far is ~0.35 ‰. Therefore, while it is possible incomplete recovery of Re during the milling process contributed to the range of fractionation found in the UOCs, the natural range of 1.06 ‰ (Miller et al., 2015; Liu et al., 2017; Dickson et al., 2020; Dellinger et al., 2020, 2021) exceeds this expected maximum fractionation. This indicates that this process alone likely does not explain the wide range in Re isotope ratios found in the UOCs.

Another possible process that could introduce isotopic variation in UOCs is contamination of the UOC with Re from within the processing facility. Rhenium contamination can occur between multiple ores that are processed at the same facility, or if Re is present in the reagents used to process the UOCs. Re contamination from reagents during the manufacturing process is possible, such as phosphomolybdate, which is used to concentrate U during the milling process. This reagent may have a high Re blank, as Re and Mo are known to concentrate together in nature. However, the Re blank of processing reagents has not been examined yet.

We can only hypothesize that processing, especially leaching, evaporation, solvent extraction, ion exchange, and precipitation could alter the Re isotopic composition of a UOC from its original ore value, but it is yet unknown to what extent this could, or does, happen. Future work constraining Re isotope fractionation factors by examining ore material and paired UOC throughout production stages would be needed to determine if there is Re isotopic fraction during processing.

4.3. Implications of Re Isotope Fractionation in UOCs

4.3.1. Rhenium as a Nuclear Forensic Tool

The wide range of Re abundances and isotope ratios within the UOC samples indicate the usefulness of Re as a nuclear forensic tool. Many elements have previously been studied in UOCs for nuclear forensic purposes (e.g., U; Brennecka et al., 2010; Varga et al., 2017; Mo; Rolison et al., 2019; Sm; Shollenberger et al., 2021; Nd; Devlin McLoughlin et al., 2023). These studies found that isotope ratios can be diagnostic of where a sample was processed and can be useful in the provenance assessment of a sample. The Re isotopic composition of a UOC is a signature of the material and useful in nuclear forensic investigations, regardless of the cause of the isotopic fractionation being natural or from the milling process. We found distinguishable differences and some overlap in the δ^{187}Re values of samples within an ore type. This information can aid in determining the source of a UOC, even when there is little additional information about a sample. For example, with the UOCs in this study, δ^{187}Re values between -0.99 to -0.15 ‰ are distinct to UOC derived from sandstone-type ore, values between -0.16 to 0.62 ‰ can represent UOC derived from either sandstone or unconformity ore, and values above 1.15 ‰ are distinct to UOC derived from QP conglomerate ore. We note that these generalizations are based on a small number of samples. As more δ^{187}Re data are collected, these interpretations will likely evolve.

Rhenium isotope ratios alone cannot definitively determine the provenance of UOC samples. This limitation is highlighted by the fact that eight of the twelve samples in this study have δ^{187}Re values that are indistinguishable within uncertainty (Fig. 2). Taken at face value, Re abundance and isotope ratio data can be paired to provide a unique geochemical signature for each mine (Fig. 3). However, using elemental abundances as a forensic signature can be dubious due to the ease in being overprinted. Instead, a powerful approach to increase the certainty in the provenance assessment of a sample is to pair data from multiple isotopic systems. Pairing δ^{187}Re data with other isotope ratio data can help identify the provenance of a sample that a single isotope system cannot distinguish by itself. For example, nine out of the twelve UOC samples in this study were analyzed for U isotopes by Brennecka et al. (2010), and five out of twelve UOC samples were analyzed for Nd isotopes by Krajkó et al. (2014) and Devlin McLoughlin et al. (2023). Plotting δ^{187}Re vs U isotope ratios (^{235}U/^{234}U and δ^{238}U; Fig. 4) provides a unique value for each sample (i.e., the position of each sample does not overlap) providing unique combinations in the plots. Plotting δ^{187}Re vs. εNd also provided unique values for each sample. These data indicate that UOCs can have unique geochemical signatures that can be used to help identify the source of the UOCs.

Additional isotope ratio data from other elements (e.g., Mo, Sm, Sr, Pb) can also be compared to Re data to further provide unique geochemical signatures for UOC samples to provide higher confidence in the assessment of a sample's provenance.

4.3.2. The Effect of δ^{187}Re Fractionation on Re-Os Dating

The Re-Os dating technique utilizes the known decay rate of ^{187}Re into ^{187}Os to determine the age of a sample. In the calculation, the Re isotopic composition of a sample has traditionally been assumed to be invariant. However, fractionation observed in this study and others (Fig. 2) has shown there is variation in Re isotope ratios and thus the Re isotope ratio should not be assumed to be invariant. This realization potentially presents an issue for Re-Os geochronology; knowledge of the Re isotopic composition of a dated samples may become necessary for accurate calculation of geochronologic ages. If a sample has an isotopic composition with a lower ^{187}Re/^{185}Re than the traditional value and is left uncorrected, it will lead to a calculated age that is younger than the true value, and vice versa for a sample with a higher ^{187}Re/^{185}Re.

Traditionally, the value of $^{187}\text{Re}/^{185}\text{Re} = 1.67394$ (Gramlich et al., 1973) is utilized for Re-Os dating, which uses Eq. (2) to calculate the age of a sample:

$$\left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_{\text{present}} = \left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_{\text{initial}} + \left(\frac{^{187}\text{Re}}{^{188}\text{Os}}\right) \text{ x } \left(e^{\lambda t} - 1\right) \tag{2}$$

where t is the age, and λ is the decay constant of ^{187}Re (1.666×10^{-11} a^{-1}; Smoliar et al., 1996; Selby et al., 2007). The calculated age of a sample depends sensitively on the ^{187}Re/^{188}Os ratio shown in Eq. (2). The ^{187}Re abundance is typically determined using isotope dilution which assumes the Re isotopic composition of a sample is invariant.

We calculated how much Re isotopic composition variations might affect Re/Os ages. We calculated the influence of 3 ‰ fractionation, (which is only slightly greater than the variation seen in our UOC samples of 2.32 ‰), on a calculated Re-Os age and associated uncertainty using IsoplotR (Vermeesch, 2018). This is a reasonable mass dependent fractionation range that can be expected to be found for Re isotope ratios in natural samples based on the range of mass dependent fractionation found in other similarly heavy redox sensitive elements (e.g., ~4 ‰ for U (Andersen et al., 2017 and references therein) and ~5 ‰ for Hg (Blum et al., 2014 and references therein)).

We find that if a sample had a 3 ‰ different isotope ratio from the traditionally assumed ^{187}Re/^{185}Re value, the calculated Re abundance using isotope dilution would be incorrect by ~1.1 %. We aggregated Re abundance uncertainty data from multiple Re-Os geochronology studies with different sample types and Re abundance ranges (e.g., Kendall et al., 2006; Markey et al., 2007; Rooney et al., 2014), and the error on Re abundance measurements generally ranges from 0.15 to 0.40 %, which does not consider natural fractionation of Re. Therefore, isotopic variations of 3 ‰ cause ages to be well outside the typical quoted uncertainty and could directly lead to miscalculated ages of sometimes millions of years, as well as increased uncertainty budgets. This demonstrates that measurement of Re isotopic ratios should be included in high-precision Re-Os ages going forward.

5. Conclusions

We present the first δ^{187}Re data from UOCs, utilizing a novel ion exchange chromatography protocol based on DGA resin to quantitatively separate Re from matrix elements. We found that UOC δ^{187}Re values derived from a variety of ore types and ages had a significant range in Re isotopic compositions from -0.99 to $+1.33$ ‰ for a total range of 2.32 ‰. This finding has greatly expanded the previously reported range of δ^{187}Re of 1.06 ‰ (from -0.97 to 0.09 ‰). The wide range in Re isotope ratios has multiple possible explanations. This range could be natural, representing the isotopic composition of the ore material, or it could be caused by the milling of ore material, or it could be a combination of both natural and industrially induced variation. We found that the isotopic composition of Re varies significantly between and within ore types and postulate that some of the variability in δ^{187}Re of sandstone ore-derived UOCs represents isotopic variability driven by redox-related deposition. Future work targeting ore material with paired UOC samples will help constrain the sources of δ^{187}Re variability in UOCs.

Regardless of the cause of the isotopic fractionation, Re isotope ratio data is a promising new tool to aid in provenance assessments of UOC found outside regulatory control due to the wide range of Re isotope ratios found so far. Rhenium isotope ratio data, when paired with other isotopic compositions of different elements produces potentially unique signatures for UOCs from different mining and milling locations. Paired comparison of Re isotope ratio data with other isotopic systems (e.g., U, Nd) can help determine the provenance of an interdicted UOC sample if there is a database of known geochemical signatures to which to compare.

CRediT authorship contribution statement

Daniel L. Sullivan: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation. **Gregory A. Brennecka:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis. **Katherine E. Grant:** Writing – review & editing, Writing – original draft, Methodology. **Ariel D. Anbar:** Writing – review & editing, Writing – original draft.

Declaration of competing interest

The authors declare no known personal relationships or financial interests that have influenced the work reported in the paper and have no other conflicts of interest to report.

Data availability

Data will be made available on request.

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Supplementary Materials

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