Measurements of rhenium isotopic composition in low-abundance samples†

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Rhenium (Re) is a trace element whose redox chemistry makes it an ideal candidate to trace a range of geochemical processes. In particular, fractionation of its isotopes $^{187}\text{Re}$ (62.6% abundance) and $^{185}\text{Re}$ (37.4%) may be used to improve our understanding of redox reactions during weathering, both in the modern day and in geological archives. Published methods for measurement of Re isotopic composition are limited by the requirements of Re mass to reach a desirable precision, making the analysis of many geological materials unfeasible at present. Here we develop new methods which allow us to measure Re isotope ratios (reported as $\delta^{187}\text{Re}/\text{Re}$) with improved precision: $\pm 0.10_{\text{norm}}^\text{2n}$ (2σ) for a mass of Re of $\sim$1 ng to $\pm 0.03_{\text{norm}}^\text{2n}$ (2σ) for a mass of Re of $>10$ ng. This is possible due to the combination of a modified column chemistry procedure and the use of $10^{13}$ Ω amplifiers for measurement via multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS). For river water samples (with Re concentrations typically $\sim 10^{-12}$ g g$^{-1}$) we design a field-based pre-concentration of Re that can be used with large volumes of filtered water (5–20 L) shortly after sample collection to provide abundant Re for isotope analysis. As a result of these developments we provide new measurements of $\delta^{187}\text{Re}$ in standards reference materials ($\delta^{187}\text{Re}$ values range from $-0.06 \pm 0.07_{\text{norm}}^\text{2n}$ to $+0.19 \pm 0.05_{\text{norm}}^\text{2n}$) and a seawater standard ($\delta^{187}\text{Re} = +0.10 \pm 0.04_{\text{norm}}^\text{2n}$), providing impetus for further exploration of the Re isotope system.

Introduction

Rhenium (Re, atomic mass 186.207) is one of the least abundant chemical elements present on Earth, with concentrations in most materials ranging from $10^{-12}$ g g$^{-1}$ (ppt) to $10^{-9}$ g g$^{-1}$ (ppb), with $10^{-6}$ g g$^{-1}$ (ppm) only in found in specific phases. Several characteristics make Re a useful element for tracking geochemical processes. Notably, its redox-dependent solubility makes it a target for tracking oxidation reactions during chemical weathering and reconstructing redox cycling in lake and oceanic sediments.

Rhenium oxidation states range from $-1$ to $+7$, with the most abundant being $+7$, $+6$ and $+4$. Rhenium is a soluble element in oxic conditions and mostly present in surface waters in the form of the oxyanion $\text{ReO}_4^{2-}$. In seawater, Re has a conservative behaviour with an average present-day concentration around 7.5 ppt. Under anoxic conditions, $\text{ReO}_4^{2-}$ is reduced to $\text{Re}^{IV}$, becomes insoluble and is removed from water either through complexation of $\text{Re}^{IV}$ with organic matter and/or incorporated into sulphides. Among the redox sensitive metals, Re has the largest enrichment factor in authigenic phases of anoxic sediments relative to the detrital background. As such, high concentrations of Re are observed in Phanerozoic sedimentary rocks formed under reducing conditions, such as black shales (average 150 ppb), relative to the upper continental crust ($\sim 0.3$ ppb) and most Precambrian sedimentary rocks ($10$–$30$ ppb). Earth’s core represents the main Re reservoir on Earth (230 ppb) and the abundance of Re in Bulk Silicate Earth (BSE, 0.35 ppb) is about two orders of magnitude lower than in carbonaceous chondrite (about 40 ppb). During magmatic processes, Re behaves as a moderately incompatible element during melting and differentiation processes.

Rhenium is composed of two naturally abundant isotopes $^{187}\text{Re}$ (62.6%) and $^{185}\text{Re}$ (37.4%). The $^{187}\text{Re}$ isotope is radioactive and undergoes $\beta$-decay to $^{187}$Os with a half-life of 4.35 × $10^{10}$ years. Following the pioneering work of Miller et al. (2009), two studies have measured the Re isotopic composition expressed as $\delta^{187}\text{Re}$, where $\delta^{187}\text{Re} = (\frac{[187]\text{Re}}{[185]\text{Re}})_{\text{std}} - 1 \times 1000$, in shales and weathered sedimentary rocks and iron meteorites. These studies have documented a total of $\sim 0.80_{\text{‰}}$ variability in $\delta^{187}\text{Re}$ values, including $\sim 0.30_{\text{‰}}$ across a chemical weathering profile in soil developed on a Devonian black shale and $0.40_{\text{‰}}$ between iron meteorites. In addition, an $ab\ initio$ calculation shows that oxidized $\text{Re}^{VII}$ species are usually enriched in $^{187}\text{Re}$ relative to more reduced $\text{Re}^{IV}$. The fractionation factor between $\text{Re}^{IV}$ and $\text{Re}^{VII}$ ($10^{-3} \times \log (\alpha_{\text{Re}^{IV}/\text{Re}^{VII}})$) could potentially vary between $-0.80_{\text{‰}}$ and $+0.50_{\text{‰}}$ depending on the degree of thiation of...
the Re\textsuperscript{VII} species.\textsuperscript{9} Overall, the existing measurements and calculations suggest that Re isotope ratios have strong potential to help track redox processes.

The previous measurements of the Re isotopic composition of materials\textsuperscript{19,20} were made by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS – Thermo Fisher Scientific Neptune, fitted with 10\textsuperscript{13} Ω amplifiers) with the combination of tungsten (W) doping and standard-sample bracketing to correct for instrumental mass bias. With that set-up, a precision of $±0.10%_{\text{iso}}$ (2σ) was achieved for a concentration of 10 ppb Re. Based on that pioneering work, many sample types were thus considered too low in Re concentration (e.g. river water, felsic rocks) to permit $\delta^{187}\text{Re}$ measurement. Here, we revisit the Re isotopic analysis by MC-ICP-MS with the aim to establish a method to measure Re isotopic composition in low abundance samples which are relevant to understanding crucial redox processes on Earth. These include grey shales with lower organic carbon contents than black shales (and Re < 1 ppb),\textsuperscript{6,7} felsic igneous rocks (Re < 2 ppb),\textsuperscript{17,21} weathered rocks and soils (Re $\sim$ ppt–ppb range),\textsuperscript{6,7,22} river waters and seawater (Re $\sim$ ppt).\textsuperscript{1,2} To do this we: (i) make use of recent mass spectrometry hardware advances (notably the development of 10\textsuperscript{13} Ω amplifiers\textsuperscript{23}) and very low uptake rate nebulizer (CF 35) which allows us to run smaller volumes at higher concentrations; (ii) explore and refine sample preparation and purification by column chemistry for solids; (iii) propose a new field pre-concentration method for river water samples; and (iv) measure and report a range of natural low Re abundance standard reference materials. We recommend repeated column chemistry procedures (loading and elution) to purify samples. The methods allow for the measurement of $\delta^{187}\text{Re}$ values to a precision of better than $±0.05%_{\text{iso}}$ (2σ) for Re mass $> 3$ ng, unlocking the vast majority of natural samples for the analysis of Re isotopic composition.

**Experimental methods**

**Reference materials and samples**

In this study, we used a wide range of SRM (Standard Reference Materials), including basalts (BCR-2, BCR-1, BHVO-2, BIR-1), sediments (MAG-1, SCO-1, NIST 1646a), granites (JG-2), peridotite (GP13), serpentinite (UB-N), andesite (AGV-1), diabase (TBD-1) and dolerite (DNC-1). We also used river samples from different locations (UK, Canada, France), a black shale and a carbonaceous chondrite sample (see ESI).

**Dissolution of solid samples**

The low Re concentration of most rock and sediment samples mean that a mass of at least $\sim$0.5 g is necessary for a precise $\delta^{187}\text{Re}$. To ensure complete re-dissolution of fluorides, a maximum aliquot mass of 0.5 g per beaker was dissolved for each sample. A volume of 3 mL 29 M HF and 3 mL of 16 M HNO\textsubscript{3} was added to each sample in PFA Teflon beakers and heated at 120 °C for at least 24 h. Following initial digestion, samples were evaporated to dryness at 80 °C and then re-dissolved in aqua regia to destroy fluorides, heated at 120 °C for 24 h before being evaporated. Finally, samples were re-dissolved in 1 M HCl. Care was taken to ensure complete dissolution and a volume of about 20 to 40 mL of 1 M HCl was required to achieve this. For samples containing refractory organic matter, a black residue was treated in 16 M HNO\textsubscript{3} and aqua regia for several days at 160 °C. Ultimately, only the most refractory organic matter (e.g. graphite) was left un-dissolved and removed from the solution by centrifugation and pipetting of the supernatant.

We tested for the potential loss of Re during heating and evaporation for 16 M HNO\textsubscript{3}, 10 M HCl, H\textsubscript{2}O, aqua regia and HClO\textsubscript{4}, at temperatures of 80, 120, 150 and 190 °C. We found no loss of Re and recovery of 100% for all reagents except for HClO\textsubscript{4}, for which there are significant evaporative losses of Re ($>85$%) at temperatures higher than 150 °C.

**Chemical separation for solid samples**

The chemical separation procedure is modified from those previously described.\textsuperscript{19,24} Polypropylene columns (inner diameter of 7.1 mm) are filled with 1 mL of AG1-X8 resin (200–400 mesh). A frit was added to the top of the resin-bed to avoid remobilization of the resin during addition of reagents. The resin is cleaned with 30 mL of 8 M HNO\textsubscript{3}, and conditioned with 5 mL of 1 M HCl. Samples are loaded on the column in 1 M HCl. At low acid concentration, Re is strongly bound to this resin,\textsuperscript{25} with the partition coefficient of Re with the AG1-X8 resin ($K_{d\text{Re}} = [\text{Re}]_{\text{resin}}/[\text{Re}]_{\text{solution}} > 100$ for HCl and HNO\textsubscript{3} concentrations $< 1$ mol L$^{-1}$. Before collecting the Re fraction, elution of the sample matrix is achieved in 3 steps: (i) addition of 10 mL of 1 M HCl, (ii) addition of 15 mL of 0.5 M HNO\textsubscript{3} and (iii) 1.5 mL of 4 M HNO\textsubscript{3} (Table 1). The Re fraction is eluted with 12.5 mL of 4 M HNO\textsubscript{3} ($K_{d\text{Re}} \sim 8–10$). The Re fraction is then evaporated at temperature of 100 to 120 °C to complete dryness and refluaxes in 16 M HNO\textsubscript{3} at 120 to 150 °C for at least 24 h. This full procedure is repeated two more times (i.e. three identical column chemistry steps) to purify the Re fraction from the residual matrix. Samples are refluaxes in 16 M HNO\textsubscript{3} after each column step to destroy resin-derived organic residues. A small aliquot (2% of the sample Re mass) is taken after 1 column pass to measure the Re concentration and after 3 column passes to check the total yield of the separation.

**Chemical separation for dissolved samples**

For dissolved Re samples (e.g. filtered river water and seawater), a volume of 1 to 20 L is usually necessary to recover enough Re for accurate $\delta^{187}\text{Re}$ ($>0.4$ ng of Re). Such volumes present significant handling and shipping issues. To overcome this, we developed a method for pre-concentrating Re in the field. River water samples are filtered at 0.2 μm (through PES Millipore filters) and collected in 20 L sterile double-lined beverage bags that are commercially available. The sample mass is measured and the bags are then connected (using a custom fitting) to a BioRad Econo-Pac\textsuperscript{®} 20 mL column filled with 2 to 4 mL of AG1-X8 resin, and passed through the column in a field laboratory (typically over a 6–10 h period). The Re-loaded columns are then capped, packaged and returned to Durham. Upon
return to the laboratory, 50 mL of 1 M HCl is passed through the resin to remove some of the matrix (and if required, to collect the SO₄ fraction for sulfur isotope analysis). Finally, the Re is collected with 30 to 40 mL of 8 M HNO₃. Using a higher HNO₃ molarity allows better recovery of the proportion of Re bound to the resin. Organic molecules from dissolved organic carbon also have strong affinity with this resin (the resin colour becomes darker for water samples with high dissolved organic carbon) and are partly eluted with Re. Therefore, to destroy these organics, the Re residue is re-dissolved in 16 M HNO₃ and refluxed for 5–7 days at 150 °C. These samples are then passed through the three steps of column chemistry separation as described for solid samples.

### Mass spectrometry

Following the method developed by Miller et al., (2009),²⁹ rhenium isotopic ratios were measured by MC-ICP MS (ThermoFisher Scientific NetunePlus without jet interface) at the Arthur Holmes Isotope Geology Laboratory, Dept. Earth Sciences, University of Durham. We use a combination of standard-sample bracketing and external normalization to tungsten (W). Following separation of Re, samples were redissolved in 0.5 M HNO₃ and a small aliquot (2% of the sample mass) was taken to measure the Re concentration by MC-ICP MS. Once the mass of Re in the remaining sample aliquot is determined, a known amount of pure W solution (ROMIL PrimAg Mono-Component Reference Solution) was added to each sample, so that the ratio (in g⁻¹) between W and Re in the sample is 20. Samples were run in 0.5 M HNO₃ and introduced using a either PFA-50 or CF 35 nebuliser together with a micro-cyclonic spray chamber. For the CF 35 nebuliser, the measured uptake rate was ~37 μL min⁻¹, giving a sensitivity of 0.26 V (¹⁸⁷Re) for a 10 ppb Re solution. In this study, we have not tested whether the use of other introduction systems (Ari- dus, Apex) could improve the sensitivity of the measurement. The standard NEPTUNE sample and H skimmer cones were used. Solution uptake time is 50 to 60 seconds with a 70 second wash time. Complete measurement of a sample (2 sample replicate analysis and 3 standards) takes ~50 minutes, consuming ~0.65 mL. The cup configuration allows simultaneous measurement of Re (¹⁸⁵Re and ¹⁸⁷Re), W (¹⁸²W, ¹⁸⁴W and ¹⁸⁸W) and monitoring of Os (¹⁸⁰Os, ¹⁸⁵Os and ¹⁸⁹Os) isotopes for possible isotopic interference (see ESI†).

Analysis were performed in low mass resolution mode (MR ~400) and consisted, like previous methods, of 25 cycles with an integration time of 16.77 s each. Whether this method is optimal for accuracy has not been fully assessed here and remains to be investigated. Hereafter, the term “analysis” is used to refer only to the 25 cycles measured on a given sample aliquot solution (one or several analyses) whereas the term “measurement” refers to the complete procedure (including digestion for solids, preparation and dilution). As Re concentrations are low in geological materials, our study used 10⁻¹³ Ω amplifiers for detectors measuring ¹⁸⁷Re and ¹⁸⁵Re isotopes and 10⁻¹¹ Ω amplifiers for other detectors. The 10⁻¹³ Ω amplifiers allow improved precision over 10⁻¹¹ Ω amplifiers on ion beams less than 0.52 V (ref. 23) (see section “Result and discussion”). Samples were typically measured at least twice (“replicate analysis” of the same purified Re solution) or more, depending upon the mass of Re available, with a bracketing standard in between (e.g. standard–sample–standard–sample–standard). All analytical sessions were carried out automatically using SC-µDX autosampler to ensure that the measurements and washouts followed a strict time sequence; necessary for interpolating and correcting for instrumental mass bias (IMB) using a standard–sample bracketing analysis method (see below).

In plasma mass spectrometry IMB is the tendency of measured isotope ratios to be biased in favour of the heavier isotope.²⁷ To a first approximation IMB is only mass dependant in MC-ICP-MS, although in reality IMB can drift slightly over time or can change as a result of instabilities in the plasma or of non-spectral interferences/matrix load on the plasma (due to residual elements).²² Rhenium has only two isotopes so IMB cannot be corrected for internally. There are two alternative approaches to correct for Re mass bias, both of which we employ in this study. It can be corrected for by doping the Re with an element of similar mass but with no isobaric masses (e.g. Ir or W)²⁰,²⁸ and normalizing to a known ratio of that element (a method referred to as “external normalization”, EN). Similar to previous studies,²⁰,²⁸,²⁹ we doped the Re with tungsten

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**Table 1**  
Column chemistry procedure

<table>
<thead>
<tr>
<th>Step</th>
<th>Acid</th>
<th>Volume (mL)</th>
<th>Elements eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin AG1-X8; 1 mL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precleaning</td>
<td>HNO₃ 8 N (twice)</td>
<td>15</td>
<td>Bulk elements</td>
</tr>
<tr>
<td>Precleaning</td>
<td>H₂O</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Equilibration</td>
<td>HCl 1 N</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Introduction</td>
<td>HCl 1 N</td>
<td>2–50</td>
<td>Residual bulk elements + Mo, Nb, Ti, Ta, Pb, Ag, W</td>
</tr>
<tr>
<td>Cleaning step 1</td>
<td>HCl 1 N</td>
<td>10</td>
<td>Residual bulk elements + Mo, Nb, Ti, Ta, Pb, Ag, W</td>
</tr>
<tr>
<td>Cleaning step 2</td>
<td>HNO₃ 0.5 N</td>
<td>15</td>
<td>Zn, Cd and Residual Pb, Ta, Nb</td>
</tr>
<tr>
<td>Cleaning step 3</td>
<td>HNO₃ 4 N</td>
<td>1.5</td>
<td>Residual Ta, Nb, Ag</td>
</tr>
<tr>
<td>Elution of Re</td>
<td>HNO₃ 4 N</td>
<td>12.5</td>
<td>Re</td>
</tr>
</tbody>
</table>

* Bulk elements are elements for which more than 85% of the elements is not fixed to the resin. It includes Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Se, Sr, Y
and corrected for Re mass bias using an exponential law using the measured $^{186}\text{W}/^{184}\text{W}$. The related equations are:

$$\frac{^{187}\text{Re}}{^{185}\text{Re}} \text{corrected} = \frac{^{187}\text{Re}}{^{185}\text{Re}} \text{measured} \times \left( \frac{m_{187}}{m_{185}} \right)^{\beta_w}$$

(1)

with:

$$\ln \left( \frac{^{186}\text{W} \times ^{188}\text{W}}{^{184}\text{W} \times ^{186}\text{W}} \text{true} \right)$$

(2)

$$\beta_w = \frac{\ln \left( \frac{m_{186}}{m_{184}} \right)_{\text{true}}}{\ln \left( \frac{m_{186}}{m_{184}} \right)_{\text{measured}}}$$

where $^{187}\text{Re}/^{185}\text{Re}_{\text{measured}}$ and $^{187}\text{Re}/^{185}\text{Re}_{\text{corrected}}$ are the measured and W-corrected Re isotope ratio, $m_{187}$ and $m_{185}$ the molar masses of each Re isotopes, $^{186}\text{W}/^{184}\text{W}_{\text{true}}$ and $^{186}\text{W}/^{184}\text{W}_{\text{measured}}$ are the real and measured W isotope ratios, while $m_{186}$ and $m_{184}$ are the molar masses of each W isotope. This method assumes that W and Re share the same degree of mass bias in the instrument (i.e. $\beta_w = \beta_{\text{Re}}$)\textsuperscript{29} and allows us to reduce both the uncertainty arising from instrumental mass bias and mitigate the influence of matrix effects.

The measured delta value expressed as below:

$$\delta^{187}\text{Re} = \left[ \frac{^{187}\text{Re}/^{185}\text{Re}}{^{187}\text{Re}/^{185}\text{Re}}_{\text{sample}} \right] \times 1000$$

(3)

Where $^{187}\text{Re}/^{185}\text{Re}_{\text{sample}}$ and $^{187}\text{Re}/^{185}\text{Re}_{\text{std}}$ can be either the W-corrected or measured ratio. Herein, we refer to the notation “$\delta^{187}\text{Re}$” as the $\delta^{187}\text{Re}$ determined by combining W-corrected (External Normalisation) and Standard-Sample bracketing (“EN-SSB method”). We refer to “$\delta^{187}\text{Re}_{\text{SSB}}$” as the Re isotopic composition determined only by SSB. Two consecutive replicate analysis of the same sample solution allow calculation of three Re isotope delta values. Following Miller et al. (2009), we use the Re standard reference material NIST SRM 989 as the normalising standard. Other pure Re standards (“HReO₄” and “NIST 3141”)\textsuperscript{29} and in-house standard solution “DURH-Re-1” are also used as secondary standards.

Results and discussion

Yield of the column chemistry separation and Re concentration measurements

We evaluate the yield of our column chemistry procedure by measuring the Re concentration of standard reference materials (SRMs) and a pure Re solution after a single pass of the column chemistry. In general, we find a good agreement (within ±10%) between our measured Re concentration values and those from the literature measured by isotope dilution\textsuperscript{19,20} (Table 2). Measured yields range from 92% to 124% with a median value of 96% ($N = 44$ digestions on 10 different SRM) with no systematic differences between rock types. This shows that HF-HNO₃ digestion and column chemistry can be used to determine Re concentration in solid material with only slightly less precision than by isotope dilution techniques. For the pure Re solution, we find yields ranging between 85% and 103%, with an average value of 98.9% ($N = 10$). This indicates that additional matrix in rock samples does not detrimentally lower the Re yield.

Efficiency of the separation

Our column chemistry procedure aims to remove inorganic and organic matrices that can create spectral and non-spectral effects and impact the accuracy of the Re isotope measurement. A large number of elements (Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Sc, Sr, Y, Cs, Nd, Hf, Th, U) are not retained by the resin (Fig. 1) and are eluted almost immediately following the initial loading step (>85%). Some elements are partly eluted during the loading step and during the initial 1 M HCl elution step (Ti, As, Zr, Mo, Sb, W). Zinc is fully retained by the resin until the 0.5 M HNO₃ step (Fig. 1) at which point it is quantitatively removed along with most of the remaining Cd (70%). About 60 to 80% of the Nb is eluted during the sample loading and 1 M HCl steps, with the remainder eluted during the 0.5 M and 4 M HNO₃ steps. Thallium is the element with the highest proportion eluted during the Re elution step (about 30% of the original thallium). Importantly for Re isotope measurement protocol, where samples are spiked with a W solution that is isotopically homogenous, W originating in the sample is almost quantitatively removed prior to the Re elution peak (Fig. 1). Compared to previous methods,\textsuperscript{19,20} the use of the 1 M HCl step prior to the 0.5 M HNO₃ allows for a more efficient removal of most chemical elements. The Re blank of the whole method (including digestion) range from 0 to 14 pg with a mean value of 3 ± 4 pg ($n = 9, 1\sigma$).

Fractionation of Re isotopes during the elution

Previous studies\textsuperscript{19,20} have shown that Re isotopes are fractionated during column chemistry and that a minimum yield of 80% is required for preventing resolvable fractionation of Re isotopes on the column. We measure $\delta^{187}\text{Re}$ as a function of the yield of the procedure for a pure Re solution (Fig. 2) and find a similar behaviour as previous work.\textsuperscript{19,20}

Field pre-concentration of Re from water samples

The Re recovery of field pre-concentration columns were checked for all water samples. For a sample set of 55 water samples, we find recovery yields ranging from 43% to 118% with a median value of 95.7%, with 48 of 55 samples having recovery yield between 75 and 120% (considering an uncertainty of ±15%). Possible fractionation of Re isotopes due to incomplete recovery of the Re pre-concentrated on the resin has been investigated by recovering various amount of pure Re solution on the 3 mL of BioRad resin used for pre-concentration (Fig. 2; filled squares). For Re recovery >30%, no Re isotopic fractionation is observed. This decreased sensitivity to fractionation compared to the 1 mL column is probably due to the different aspect ratio of the column used for the field and/or the different eluent concentration (here 8 M HNO₃).
Evaluation of analytical errors

Here we discuss the different sources of error during Re isotopic measurement by MC ICP-MS. We refer to the “internal error” as the standard error (SE, in \(2\sigma\)) of the 25 cycles of 16.77 second-integration periods (corresponding to one “analysis”). The “intermediate error” is the standard deviation (SD, in \(2\sigma\)) of repeated analysis of the same solution, (here 2 sample analysis and 3 bracketing standards, giving 3 measured \(\delta^{187}\)Re). This within-run-precision will be influenced by mass bias instability over tens of minutes to an hour. Finally, the “external error” corresponds to the standard deviation (SD, in \(2\sigma\)) of several measurements of a given solid or dissolved material (including digestion for solids, preparation and dilution) over an extended period of time. This between-run-precision will be influenced by day-to-day differences in instrumental plasma conditions and by sample preparation steps for samples.

There are two major sources of noise that influence the internal error: counting statistics and the Johnson–Nyquist noise.\(^{34,36}\) The internal error for a given signal intensity of repeated analysis of the same solution, (here 2 sample analysis and 3 bracketing standards, giving 3 measured \(\delta^{187}\)Re). This within-run-precision will be influenced by mass bias instability over tens of minutes to an hour. Finally, the “external error” corresponds to the standard deviation (SD, in \(2\sigma\)) of several measurements of a given solid or dissolved material (including digestion for solids, preparation and dilution) over an extended period of time. This between-run-precision will be influenced by day-to-day differences in instrumental plasma conditions and by sample preparation steps for samples.

Table 2 Results for Re concentration measurements

<table>
<thead>
<tr>
<th>SRM name</th>
<th>Mass digested per sample (mg)</th>
<th>[Re] (ppb) (\pm 2)SD (in %)</th>
<th>(N) measurements</th>
<th>[Re] (ppb) (\pm 2)SD (in %)</th>
<th>(N) measurements</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR-2</td>
<td>60 to 514</td>
<td>11.56</td>
<td>6.4</td>
<td>8</td>
<td>12.60</td>
<td>15.9</td>
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<tr>
<td>BCR-1</td>
<td>480 to 653</td>
<td>0.81</td>
<td>9.6</td>
<td>9</td>
<td>0.84</td>
<td>30</td>
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<tr>
<td>UB-N</td>
<td>466 to 698</td>
<td>0.20</td>
<td>14.3</td>
<td>9</td>
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<td>MAG-1</td>
<td>172 to 559</td>
<td>3.65</td>
<td>7.3</td>
<td>6</td>
<td>3.91</td>
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<td>BHVO-2</td>
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<td>12.8</td>
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<td>0.54</td>
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<td>BIR-1</td>
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<td>1</td>
<td>0.65</td>
<td>2</td>
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<td>JG-2</td>
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<td>1</td>
<td>1</td>
<td>0.016</td>
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<td>GP-13</td>
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<td>1</td>
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<td>11.96</td>
<td>8.4</td>
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<tr>
<td>NIST 1646a</td>
<td>515</td>
<td>1.99</td>
<td>1</td>
<td>1</td>
<td>1.2</td>
<td>10.4</td>
</tr>
</tbody>
</table>

Fig. 1 Elution curves of chemical elements and Re for two standard materials. Element concentrations were measured by quadrupole ICP-MS. Bulk elements are shown in Table 1.

Fig. 2 Rhenium isotope composition of pure Re solution (NIST-SRM989) as a function of the proportion of recovery from (i) field-based columns (black squares) and (ii) laboratory columns (grey circles). White diamonds are from Miller et al., (2009).\(^{19}\) The green area is the \(\pm 0.05\)\% long-term external reproducibility of pure Re solution at 5 ppb Re concentration.
corresponds to the sum of these two sources of error. The counting statistics can be predicted following the Poisson distribution.\textsuperscript{27,34,35} The relative standard error (RSE) in the isotope ratio due to counting statistics (\(\sigma_{\text{counting statistics}}\)) is:

\[
\sigma_{\text{counting statistics}} = \sqrt{\frac{n_{187} + n_{185}}{n_{187} \times n_{185}}}
\]  

(4)

Where \(n_{187}\) and \(n_{185}\) represent the total number of ions collected for each Re isotope for a given period of time, in this case analysis. The latter are calculated as:

\[
n_{187} = \frac{V_{187}}{R \times \text{Gain}} \times t \times 6.241 \times 10^{18}
\]  

(5)

Where \(R\) is the resistor amplifier (here 10\(13\) \(\Omega\)), “Gain” the gain (0.01), “\(V_{187}\)” the voltage for 187Re, “\(v\)” is the total integration time of the measurement (25 cycles of 16.77 seconds) and 6.241 \(\times 10^{18}\) is the conversion factor for amperes to number of ions. An intensity of 0.1 V measured on a 10\(13\) \(\Omega\) amplifier, with a gain of 0.01, for 1 second corresponds to 10\(\text{-}12\) A, which gives a number of ions \(n = 6.24 \times 10^{5}\) cps V\(^{-1}\). The Johnson–Nyquist noise corresponds to the fluctuation of the current in the resistor due to the thermal agitation of electrons:

\[
V_{jn} = \sqrt{\frac{4 \times k \times R \times T}{t}}
\]  

(6)

Where “\(k\)” is the Boltzman constant, \(R\) is the amplifier resistor value, \(T\) is the amplifier temperature in Kelvin, which for the Neptune is 319 K. Assuming that both detectors have the same amplifier, the Johnson noise error\textsuperscript{4,35} is:

\[
\sigma_{\text{Johnson noise}} = \sqrt{(V_{jn} \times \text{Gain} / V_{187})^2 + (V_{jn} \times \text{Gain} / V_{185})^2}
\]  

(7)

We can see from eqn (7) that an increase of the resistor amplifier from 10\(11\) to 10\(13\) \(\Omega\) results in an increase of the Johnson–Nyquist noise by a factor of 10, whereas at the same time the gain increases by a factor 100, which implies that the signal/noise ratio is improved by a factor of 10 using 10\(13\) \(\Omega\) amplifiers.\textsuperscript{34} Finally, the total internal error, corresponding to the sum of the counting statistics noise and the Johnson noise is calculated\textsuperscript{14,35} as:

\[
\sigma_{\text{internal error}} = \sqrt{\sigma_{\text{Johnson noise}}^2 + \sigma_{\text{Counting statistics}}^2}
\]  

(8)

These theoretical calculations show that for a signal intensity higher than 0.5 V, the only significant source of uncertainty is the counting statistics. In this case, the SE is the same for the 10\(11\) \(\Omega\) and 10\(13\) \(\Omega\) amplifiers (Fig. 3). Below 0.5 V, the role of Johnson–Nyquist noise increases for the 10\(11\) \(\Omega\) amplifier but remains negligible for the 10\(13\) \(\Omega\) amplifier (Fig. 3). The difference between the SE (2\(\sigma\)) of 10\(11\) \(\Omega\) and 10\(13\) \(\Omega\) amplifier is small (<0.01\text{%}) for 187Re intensity >0.3 V, but significant (0.04\text{%}) for 187Re intensity of 0.1 V, and very high (>0.10\text{%}) for intensity <0.1 V. Our measurements of pure Re solutions agree well with theoretical predictions and confirm the lower SE at a given intensity for 10\(13\) \(\Omega\) relative to 10\(11\) \(\Omega\) amplifiers. No difference in the measured internal error was observed between pure Re solutions and samples processed through column chemistry. Hence, the use of 10\(13\) \(\Omega\) amplifiers acts to significantly improve the internal error for small beam intensities, i.e. <0.2 V. The internal error for 1 ng of Re is less than 0.10\text{%} for 10\(13\) \(\Omega\) amplifiers but higher than 0.20\text{%} for 10\(11\) \(\Omega\) amplifiers.

We also evaluated the variability of the intermediate error as a function of the 187Re beam intensity (Fig. 3B). We observe no significant difference between pure Re solutions and samples (which include column chemistry). The average values of intermediate errors increase with decreasing 187Re beam intensity. The average intermediate errors for a given 187Re beam intensity are similar to internal errors, showing that the

![Fig. 3](image-url) Standard error and deviation on 187Re/185Re ratio (as 2\(\sigma\)) as a function of the 187Re beam intensity (in V). In (A) are the predicted trends (see main text) and data measured with 10\(11\) and 10\(13\) \(\Omega\) amplifiers on both Re isotopes. (B) Average intermediate and external error calculated every 0.05 V for a HReO\(_4\) solution measured over the course of three years (see Table 3). The relationship between the beam intensity (\(I_{\text{Re}}\)) and the mass of Re required (\(m_{\text{Re}}\), in ng) for two repeated analysis of each sample is \(m_{\text{Re}} = 24.866 \times I_{\text{Re}}\).
internal errors can explain the variability between consecutive replicate analysis. To evaluate the long-term reproducibility (i.e. external error) associated to our \( \text{Re} \) isotope measurements, we repeatedly measured a pure \( \text{Re} \) solution (HReO\(_4\)) at various \( ^{187}\text{Re} \) beam intensity over the course of three years (Table 3). We calculated the external error as 2 SD of: (i) of individual analysis of HReO\(_4\); and (ii) averages of consecutive replicate analysis of HReO\(_4\) solutions. No significant difference is observed between the internal, intermediate and external error for replicate analysis (Fig. 3B). However, the external error is higher than the internal error on individual analysis. This shows that, on average, the internal errors can explain the variability between consecutive replicates, and between long-term repeated measurements. There is a tradeoff between running a sample once (1 analysis) at higher concentration (with issues to consider, e.g. potential for short-term blockage or instability) and running a sample multiple times (several analysis) at lower concentration. Here we choose to analyse each sample twice consecutively and use the relationship between the external error and the \( ^{187}\text{Re} \) beam intensity (red curve on the Fig. 3B) to determine the “overall uncertainty” for each sample.

### Influence of \( \text{W}/\text{Re} \) ratio and intensity matching

Previous study\(^{19} \) doped samples to \( \text{W}/\text{Re} \) ratio of 2. However, in our case, since we measured \( \text{Re} \) isotopes at lower \( \text{Re} \) concentration with \( 10^{13} \) \( \Omega \) amplifiers on \( \text{Re} \) isotope cups and \( 10^{11} \) \( \Omega \) amplifiers on \( \text{W} \) isotope cups, we required a higher \( \text{W}/\text{Re} \) ratio. A \( \text{W}/\text{Re} \) ratio of 2 would result in an internal error on the \( ^{186}\text{W}/^{184}\text{W} \) higher than that for the \( ^{187}\text{Re}/^\text{186}\text{Re} \) ratio and this would be propagated onto the latter through the mass bias correction. Instead, we used a \( \text{W}/\text{Re} \) ratio of 20, so that even at very low \( \text{Re} \) concentration, the internal error on the \( ^{186}\text{W}/^{184}\text{W} \) is at least three times lower than the internal error on the \( ^{187}\text{Re}/^{185}\text{Re} \). In addition, having a high \( \text{W}/\text{Re} \) ratio means that the contribution of residual \( \text{W} \) from the sample is lower. To ensure that this \( \text{W}/\text{Re} \) ratio does not create problems (in terms of abundance sensitivity or hydrides), we tested different \( \text{W}/\text{Re} \) ratios (1, 5, 10, 20 and 40) for two different \( \text{Re} \) concentrations (1 ppb and 5 ppb) and found no differences in precision and accuracy for \( \text{W}/\text{Re} \) ratios ranging from 5 to 40 (see ESI).

Differences in the concentrations between the sample and bracketing standard can potentially influence isotopic measurements. To test this, we measured pure rhenium solutions prepared with distinct \( \text{Re}/\text{W} \) ratio relative to the \( \text{Re}/\text{W} \) of the bracketing standard. We observe that \( \delta^{187}\text{Re} \) values are offset by more than 0.05\(^{\circ}\) for a ratio mismatch of more than 40% (Fig. 4). This shows that is crucial to match within 10% the \( \text{Re}/\text{W} \) of the measured sample with that of the bracketing standard. The reasons for this effect may be due to different contributions of hydrides or \( \text{W} \) backgrounds.

### Matrix effects and accuracy of the measurements

Residual inorganic and/or organic matrices following column separation can impact the accuracy of isotope measurement.\(^{27,28} \) We compared the measured \( \delta^{187}\text{Re} \) after one, two, three and four repeated column separations (Fig. 5). This test illustrates

---

**Table 3** Results of pure \( \text{Re} \) solution reference standard measured

<table>
<thead>
<tr>
<th>Standard</th>
<th>( ^{187}\text{Re} ) (%)</th>
<th>( ^{187}\text{Re}/^{185}\text{Re} ) (%)</th>
<th>( ^{186}\text{W}/^{184}\text{W} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HReO(_4)</td>
<td>0.45–0.50</td>
<td>0.48</td>
<td>0.22</td>
</tr>
<tr>
<td>187ReSRM989</td>
<td>0.40–0.45</td>
<td>0.41</td>
<td>0.23</td>
</tr>
<tr>
<td>DURH-Re-1</td>
<td>0.45–0.50</td>
<td>0.48</td>
<td>0.22</td>
</tr>
<tr>
<td>SRM 3141</td>
<td>0.45–0.50</td>
<td>0.48</td>
<td>0.22</td>
</tr>
<tr>
<td>DURH-Re-1</td>
<td>0.45–0.50</td>
<td>0.48</td>
<td>0.22</td>
</tr>
</tbody>
</table>
that the measured $\delta^{187}\text{Re}$ can change as a function of number of column passes but how it does so is somewhat dependent on sample type. For BCR-2 (basalt), the $\delta^{187}\text{Re}$ values are lower for two column passes relative to one, but similar for two and three column passes. For a chondrite (Allende), we also observe no difference in $\delta^{187}\text{Re}$ between the second and fourth column passes on the same aliquot. For a seawater reference material (OSIL Atlantic seawater standard), the $\delta^{187}\text{Re}$ for three and four column passes are identical, but lower than for two column passes. For one river water (River 2 Canada), the $\delta^{187}\text{Re}$ is significantly higher for 1 column pass relative to the value measured after 2 or more passes. For others (River 1 and 2 Canada), there is a small decrease of the $\delta^{187}\text{Re}$ value after three passes relative to two, although this is not observed for every river sample (e.g. River UK and River 3 Canada).

Overall, these tests reveal two things: (i) in general, the $\delta^{187}\text{Re}$ values are unchanged after three column chemistry separations; (ii) the materials which continue to show a change in $\delta^{187}\text{Re}$ after more than two repeated separations are materials that originally contain organic matter (river water and shales). To test whether the amount of remaining inorganic matrix can affect the accuracy of $\delta^{187}\text{Re}$ measurement, we performed a series of tests where a Re standard solution, doped with various elements [Al, Fe, Mg, Nb, Zr, Ta, Mo, Zn, U, Hf] at different concentrations, covering a range of value of X/Re (where X is the doped element), was measured. We observed that over the range of concentrations of dopant tested, there is no effect, within uncertainty, on the accuracy of the $\delta^{187}\text{Re}$ value (see ESI†). In addition, we used a granite SRM (USGS “G-2”) with a very low Re concentration (11 ppt) that we doped with a known mass of $^{187}\text{Re}$-rich standard solution DURH-1 ($0.44 \pm 0.02\%_{\text{rel}}$). With great care, we set-up a procedure so that the contribution of Re from the sample is negligible ($<0.6\%$, see ESI†). This modified granite SRM was passed through column chemistry (3 times) and measured as a normal sample and returned the same value as pure DURH-1 (Fig. 6). These tests show that our column procedure is optimal for removing effects caused by an inorganic matrix.

Organics that influence isotopic measurement can originate from: (i) the resin or (ii) the sample. Matrix effects caused by resin degradation have been documented for other isotope systems.$^{37,38}$ In this study, we systematically treat the column residue with concentrated HNO$_3$ at 130–150 °C for 24 h before isotope measurement. Measurements of pure Re solutions processed and non-processed through column chemistry return identical $\delta^{187}\text{Re}$ values (Table S4, ESI†) suggesting that any residual organic molecules derived from the resin do not affect the measurement. We note though that for some of these tests, abrupt changes in the $^{186}\text{W}/^{184}\text{W}$ mass bias are observed, leading to inaccurate $\delta^{187}\text{Re}_{\text{SSB}}$ and ($\delta^{187}\text{Re}_{\text{SSB}}-\delta^{187}\text{Re}$) values up to $+0.35\%_{\text{rel}}$, but correct $\delta^{187}\text{Re}$. This shows that matrix effects caused by residual resin-derived organics are adequately corrected for using W normalization.

Resin AG1-X8 is a cationic resin for which organic molecules (negatively charged) have a high affinity. Adsorption of organic molecules to the resin is evidenced by a change in the colour (orange to dark) of the resin. Some of the organics are eluted in
4 M HNO₃, at the same time as Re, observed as a yellowish color of the solution and the size/colour of the residue. These organics could potentially create interferences on the Re isotopic measurement and influence the elution volume of Re (e.g. competition for binding sites on the resin). To assess the role of organic matter we used two samples (New Zealand soils with 1 and 6% organic carbon) that have a very low Re concentration (<35 ppt) and several shale-type Re-free matrix (by mixing volume cuts before and after Re elution peak, see ESI†) and doped them with Re solution DURH-Re-1. Following three column chemistry separations, we measured δ¹⁸⁷Re values respectively which are in agreement within uncertainty with the value of the DURH-Re-1 standard (Fig. 6). Collectively, this shows that our column procedure successfully remove effects caused by sample-derived organic matrix.

Application to reference materials and assessment of data quality

The δ¹⁸⁷Re values of several reference materials (BCR-2, BHVO-2, UB-N, BIR-1, MAG-1, SDO-1, OSIL Atlantic Seawater) have been determined (Table 4). The variability in δ¹⁸⁷Re values defined by these standards is about 0.28‰ relative to pure Re solution. Since there are very few reference materials that have been measured for δ¹⁸⁷Re, it is of prime importance to assess the accuracy of the measurements. Our analysis of NIST 3141 and HReO₄ return δ¹⁸⁷Re values respectively of 0.28 ± 0.03‰ and 0.22 ± 0.03‰ in agreement with published values.²⁹ The δ¹⁸⁷Re value we obtain for the SDO-1 standard, δ¹⁸⁷Re = 0.19 ± 0.03‰ also matches previously published value.²⁹ These results are encouraging for accurate analysis, however in future a wider range of materials will need to be cross-calibrated between laboratories for a more thorough assessment.

Perspectives for the measurement of δ¹⁸⁷Re in geological samples

The first Re isotope study²⁹ achieved precision of ±0.10‰ for 10 ng of Re. From this, the authors concluded that Re isotope measurements would be limited only to Re-rich samples (such as black shales or sulfide ores). Here, our external reproducibility is ±0.04‰ for 5 ng of Re (Fig. 3) based on the use of 10¹⁵Ω amplifiers in wet plasma conditions (micro-cyclonic chamber). There are potential alternative methods that could be used to deliver this improvement, or further refine it. A desolvator (Aridus, Apex) combined with a jet sample cone and X-skimmer cone could lead to a further significant increase of the sensitivity for Re. However, there are concerns regarding the Re beam stability in dry plasma conditions and the possibility of Re isotope fractionation on the desolvator membrane.²⁹ Future studies should assess whether these additional changes to the sample introduction and/or interface could allow further reduction in the volume of sample required for making precise Re isotopic measurements.

Irrespective of any refinements to the sample introduction and interface, the modified column chemistry and analytical advances we have made allow a large range of geological materials to be measured at high precision (Fig. 7). For instance, for most organic rich shales, we estimate that only ~0.1 g of sample is required for a precision of ±0.04‰. For igneous rock samples

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<table>
<thead>
<tr>
<th>Reference material</th>
<th>δ¹⁸⁷Re (‰)</th>
<th>Overall uncertainty (±2 SD)</th>
<th>External error (±2 SD)</th>
<th>Number of measurements</th>
<th>Intermediate error (±2 SD)</th>
<th>Internal error (±2 SE)</th>
<th>Mass Re per analysis (ng)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSIL (Atlantic seawater)</td>
<td>0.10</td>
<td>0.04</td>
<td>0.02</td>
<td>4</td>
<td>0.05</td>
<td>0.05</td>
<td>3.9</td>
</tr>
<tr>
<td>MAG-1 (marine mud)</td>
<td>−0.06</td>
<td>0.05</td>
<td>0.07</td>
<td>3</td>
<td>0.05</td>
<td>0.05</td>
<td>4.2–5.5</td>
</tr>
<tr>
<td>BHVO-2 (basalt)</td>
<td>−0.06</td>
<td>0.06</td>
<td>0.07</td>
<td>2</td>
<td>0.06</td>
<td>0.06</td>
<td>2–2.5</td>
</tr>
<tr>
<td>BIR-1(basalt)</td>
<td>−0.06</td>
<td>0.07</td>
<td>0.02</td>
<td>1</td>
<td>0.06</td>
<td>0.06</td>
<td>0.9</td>
</tr>
<tr>
<td>BCR-2 (basalt)</td>
<td>−0.01</td>
<td>0.04</td>
<td>0.02</td>
<td>5</td>
<td>0.05</td>
<td>0.04</td>
<td>4.9–12.2</td>
</tr>
<tr>
<td>CV3 Allende (chondrite)</td>
<td>−0.01</td>
<td>0.03</td>
<td>0.01</td>
<td>1</td>
<td>0.01</td>
<td>0.01</td>
<td>21</td>
</tr>
<tr>
<td>SDO-1 (black shale)</td>
<td>0.19</td>
<td>0.05</td>
<td>0.03</td>
<td>2</td>
<td>0.01</td>
<td>0.04</td>
<td>3–12</td>
</tr>
<tr>
<td>UB-N (serpentine)</td>
<td>0.00</td>
<td>0.08</td>
<td>1</td>
<td>1</td>
<td>0.04</td>
<td>0.08</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Fig. 7 Sample mass required (in g) as a function of the Re concentration of geological materials for different measurement precisions. Rhenium concentration data from published work.²⁴,²¹
(e.g. Mid-Ocean Ridge Basalts, MORB), we estimate that ~1–5 g would be required for a precision of ±0.04‰. For river waters, a large volume of sample (~1 to 20 L) is still required because most rivers have dissolved Re concentrations in the ppt range (Fig. 7). Our field pre-concentration method addresses this. Instead of transporting many kilograms of filtered water, we are able to concentrate ~5–10 ng of Re onto a few mL of resin and subsequently recover Re for precise isotopic analysis. The required precision for any isotopic analysis will depend on the range of δ187Re values expected in the samples undergoing analysis. So far, the range of measured δ187Re in geological materials is ~–0.80‰ to ~0.03‰, a range much larger than the analytical precision. Along with the method developments described here which make the vast majority of natural samples available for analysis (Fig. 7), these calculations provide impetus for further exploration of the Re isotope system.

Conclusions

Here we provide new methods to measure the isotopic composition of Re in a wide range of solid and liquid samples. The main points are:

- An improved precision via MC-ICP-MS afforded by the use of 10^11 Ω amplifiers on 185Re and 187Re.
- The use of W doping, matching W/Re ratios of samples and standards, and standard-sample bracketing allows for the correction of instrumental mass bias and some matrix effects.
- The importance of column chemistry separation, and here we provide evidence that three repeated separations are necessary.
- The use of a field-based pre-concentration of Re for river water samples, which makes the analyses of river waters feasible.

Combining these approaches, we are able to report an improved precision on δ187Re measurements for a lower required mass of Re (±0.10‰ for a mass of Re of ~1 ng to ±0.03‰ for a mass of Re of >10 ng) compared to previous studies.19,20 We have analysed a range of solid geological reference materials, and a seawater standard, and observe variability of 0.28‰. The approaches here open up studies of Re isotopic fractionation, in particular opening up the potential of Re isotopes as a proxy for oxidative weathering, and for reconstruction of past redox cycling.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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