Electronic Supporting Information

Measurements of Rhenium Isotopic Composition In Low-Abundance Samples

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Cup configuration:

Cup	L4	L3	L2	L1	C	H1	H2	H3	H4
Main isotope	-	^{183}W	^{184}W	^{185}Re	^{186}W	^{187}Re	^{188}Os	^{189}Os	-
Collector	-	10^{11}	10^{11}	10^{13}	10^{11}	10^{13}	10^{11}	10^{11}	-

Figure S1: Cup configuration used for simultaneous measurement of Re and W isotopes

Tests to determine the influence of residual inorganic matrix on Re isotopes:

To determine the efficiency of the separation method for removing inorganic matrix, we measured the ratio between chemical elements and Re for different types of materials (chondrite, basalt, shale, river water) having distinct Re concentration (Figure S2). For basalt SRM BCR-2 and shale SRM MAG-1, we can see that after 2 column passes, the ratio X/Re (in g/g) for most chemical elements is < 50. The highest residual concentration elements being Al, Nb, Zr and Mo. For BCR-2, the second column chemistry lead to significant further removal of Al, Mg, Fe and Tl while the X/Re ratio for most of other elements does not significantly changed between the first and second column. For river waters, the X/Re ratio after two column separation is lower than 1 for most of the elements showing that inorganic matrix residue is even significant than in the rock samples.

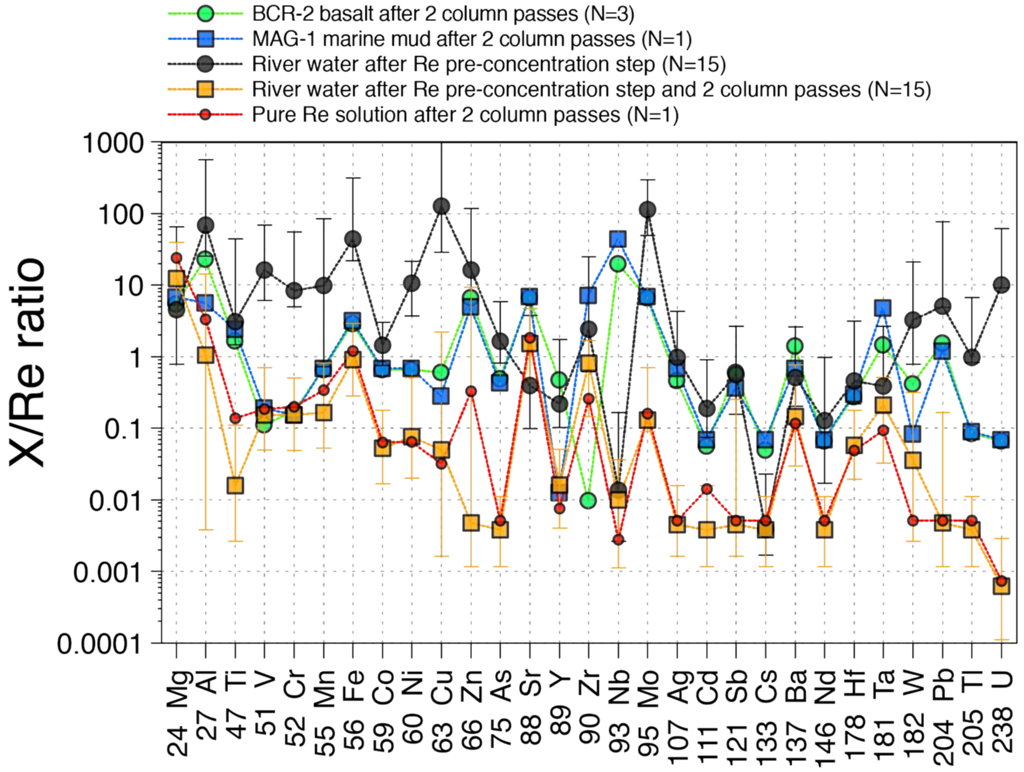

Figure S2. X/Re ratio values (with X any chemical element, in g/g) measured in Re fraction after column chemistry for different type of materials (Basalt, Marine mud, river water, pure Re solution). Are represented the average value for several independent samples or digestions (except for MAG-1, only 1 measurement) with the error bar corresponding to the SD of all the measurements.

Using these results, we performed a series of tests where a Re standard solution was 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) corresponding to the X/Re ratios measured in solutions after 2 column passes. Results are presented in figure SXX and show no significant influence of inorganic elements on the measured Re isotopic composition.

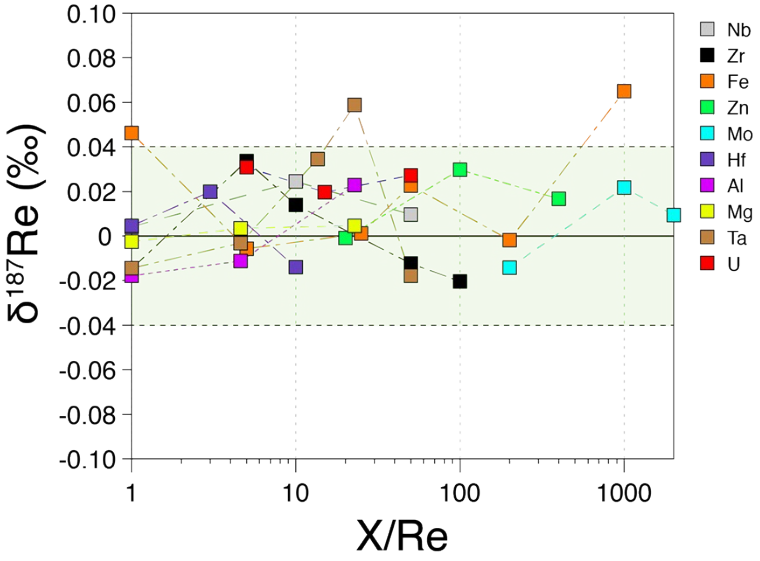

Figure S3. δ^{187}Re (relative to NIST-SRM989) as a function of the ratio between chemical elements (Nb, Zr, Fe, Zn, Mo, Hf, Al, Mg, Ta and U) and Re. All measurements were performed for beam intensity of 0.2V on ^{187}Re (corresponding to 5 ng of Re).

Influence of W/Re ratios:

The influence of the amount of tungsten external standard added to the sample for isotope measurement (W/Re ratio) was tested by measuring HReO4 standard doped with various amount of W (the bracketing standard have the same W/Re ratio) for two different Re concentrations, 10 and 1.5 ppb Re (Figure SXX). We observe no influence of the W/Re ratio for values ranging from 5 to 40.

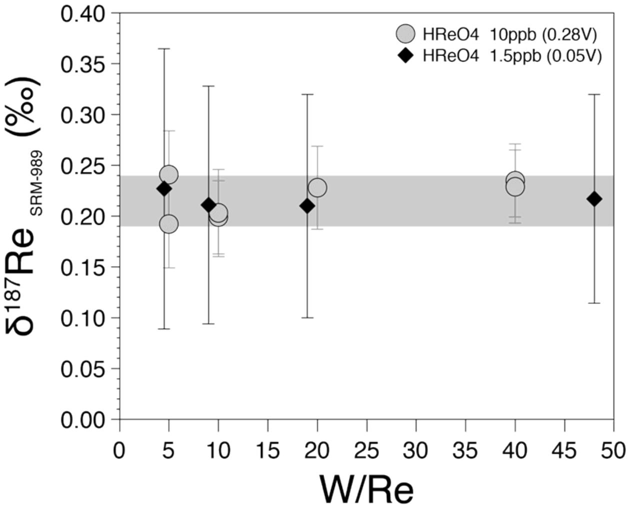

Figure S4. δ^{187}Re (relative to NIST-SRM989) as a function of the W/Re used for measurement (W standard added after column chemistry, same W/Re between bracketing standard SRM 989 and HReO4 measured standard. The Grey shaded area corresponds to the average δ^{187}Re of HReO4.

Assessment of data quality:

One way to assess data quality is to compare the δ^{187}Re value calculated with the Standard-sample bracketing method ($\delta^{187}\mathrm{Re}^{\mathrm{SSB}}$) with that calculated by both W-corrected and SSB methods (δ^{187}Re). External normalization to W is used to correct for both the changes in the plasma conditions and matrix effects. In general, we find that the external error for the SSB method of mass bias correction is greater than for the combined EN-SSB method and relatively independent of the Re concentration but quite sensitive to instrumental stability (plasma, nebuliser uptake stability, spray chamber) during any given analytical session. Thus, correcting for changes of the mass bias using combination of W-normalization and SSB gives more accurate results.

In the case of relatively stable or constant mass bias (and in the absence of matrix effect) the δ^{187}Re determined by $\delta^{187}\mathrm{Re}^{\mathrm{SSB}}$ and δ^{187}Re should be equal ($\delta^{187}\mathrm{Re}^{\mathrm{SSB}} - \delta^{187}\mathrm{Re} = 0$). In the case of a non-stable mass-bias, which happened during some of our sequences, we measure a maximum ($\delta^{187}\mathrm{Re}^{\mathrm{SSB}} - \delta^{187}$Re) of +0.27‰ and a minimum of -0.14‰, showing that plasma instabilities can lead to inaccurate $\delta^{187}\mathrm{Re}^{\mathrm{SSB}}$ but correct δ^{187}Re values. For geological samples, two BCR-2 measurements and one soil doped with Re of known composition yielded $\delta^{187}\mathrm{Re}^{\mathrm{SSB}} - \delta^{187}\mathrm{Re} = +0.30$‰ (See supplementary tables XX), but correct δ^{187}Re values. These results actually illustrate the importance of applying W correction as this corrects for small variations in mass bias, presumably resulting from matrix effects, that SSB alone would not correct for. Nevertheless, as a precautionary measure we reject any measurements for which ($\delta^{187}\mathrm{Re}^{\mathrm{SSB}} - \delta^{187}$Re) exceeds 0.30‰.

Preparation of Re-free matrix standards for Re isotope accuracy tests:

To assess the accuracy of our Re isotope measurements, we prepared two Re-free typical geological matrix by collecting volume cuts before and after Re elution peaks for different materials. These cuts were then re-combined, evaporated and then treated like a "normal" sample, i.e. passed three times through column chemistry. After three column passes, a small aliquot (2% of sample mass) was taken to check the absence of Re. Then, a known amount of ^{187}Re rich (i.e. very different δ^{187}Re relative to current range of measured δ^{187}Re for geological materials) in-house standard DURH-Re-1 was added to the “matrix” sample and the δ^{187}Re was measured.

Matrix 1: a mass of 4.5 g of different river sediment samples (original Re concentration of ~0.2 ppb) containing < 1% TOC, doped with 12 ng of DURH-Re-1 standard.

Matrix 2: a mass of 0.4 g of Posidonia Shale sample from NW Germany (original Re concentration of ~45 ppb) containing > 1% TOC, doped with 2.5 ng of DURH-Re-1 standard.

One limitation of the previous test is that it does not account for the fact that some elements or organic molecules may have identical behaviour to Re during our column chemistry method (i.e. elution from the column only with 12 mL of 4M HNO_3) and create matrix effect which would bias δ^{187}Re measurements. To test this, we prepared an additional set of matrix materials corresponding to samples “naturally” containing low Re concentration and doped with DURH-Re-1:

Matrix 3: a mass of 1.5 g of Granite SRM “G2” (Re concentration of 0.011 ppb) doped with 3 ng of of DURH-Re-1 standard.

Matrix 4: a mass of 1.5 g of New Zealand soil sample NZ14-54 (Re concentration of 0.036 ppb) and containing Total Organic Carbon (TOC) of 1.3%, with 3 ng of of DURH-Re-1 standard.

Matrix 5: a mass of 1.5 g of New Zealand soil sample NZ14-62 (Re concentration of 0.021 ppb) and containing Total Organic Carbon (TOC) of 7.5%, with 3 ng of of DURH-Re-1 standard.

Matrix 6: a mass of 2.5 g of New Zealand soil sample NZ14-54 (Re concentration of 0.036 ppb) and containing Total Organic Carbon (TOC) of 1.3%, doped with 2.5 ng of of DURH-Re-1 standard.

Samples and materials used for column chemistry tests:

The samples used for testing the effect of the number of column passes on the measured Re isotopic composition (Fig. 5) are:
“River UK” = River Wear sampled in Durham
“River 1, 2, 3 Canada” = Rivers from the Mackenzie River basin (Canada)
“River France” = Small river in the French Alps from the Rhone river basin (France)
“Black shale” = Posidonia Shale sample from NW Germany
“Chondrite” = Allende Chondrite
“Basalt” = BCR-2 basalt reference material

Supplementary tables:

We provide two spreadsheets (one with simplified tables, the other one with raw data) with tables and supplementary tables:

- **Table S1**: Tests with different W/Re of the bracketing standard relative to the sample (here the bracketing standard and the “sample” are the same solution).
- **Table S2**: Tests of Re isotope fractionation during incomplete elution through column chemistry for the column containing 1 mL AG1-X8 resin and for large column containing 3 mL AG1-X8 resin used for pre-concentration of Re from water sample on the field.
- **Table S3**: Doping tests with different elements and various X/Re ratio (the doped standard and the bracketing standard are the same solution), data corresponding to the figure SXX.
- **Table S4**: Results of standard reference materials and matrix test material measured for Re isotopes. Each line corresponds to a single complete measurement (from digestion to Re isotope analysis).
- **Table S5**: Influence of the W/Re of both bracketing standard and measured solution on the measured Re isotopic composition (for two concentration, 10 ppb and 1.5 ppb)
- **Table S6**: Results for Re concentration measurements for a wide range of SRMs