Supplementary information for 'The rhenium isotope composition of modern Atlantic Ocean seawater'

1. Preparation and calibration of the Royal Holloway ^{185}Re spike solution

An aliquot of ^{185}Re-enriched metal powder was obtained from Oakridge National Laboratory (lot no. 134991). The powder was transferred into a clean Teflon bottle using concentrated nitric acid and placed on a hotplate at 70°C for 2 days to allow the spike powder to dissolve fully. The solution was then diluted to a volume of ~1 litre with 3% nitric acid.

The ^{187}Re/^{185}Re ratio of the spike solution was calibrated by sample-standard bracketing to NIST SRM 989. Both solutions were diluted to 200 ppb and analysed alternatively using a Neptune Plus MC-ICP-MS in low-resolution mode and wet (SIS spraychamber) sample introduction. Each analysis consisted of 60 cycles of 8.4 s collected in a single block. Measured voltages were corrected for acid blanks, which were measured for 10 cycles of 8.4 s immediately prior to each sample measurement. In practice, all acid blanks constituted <0.01 % of the sample voltage and made little difference to the final ratios. NIST SRM 989 and the ^{185}Re spike solution were measured alternatively. Instrumental mass fractionation (f) was corrected using the exponential mass bias law by referencing the measured NIST 989 ratios to the certified ^{187}Re/^{185}Re of 1.674 (Gramlich et al., 1973). The average f of bracketing NISTs were applied to intervening spike measurements. The solution concentrations were sufficient to obtain signals of ~100mV on mass 187 of the spike solution.

The concentration of the spike was calculated by reverse isotope dilution by mixing the concentrated spike solution with aliquots of either of two separate gravimetrically-prepared Re solutions. These solutions were both prepared from H Cross Company high-purity Re filament ribbon. Immediately before weighing, the metal was immersed completely in concentrated HCl for ~1 minute, and subsequently rinsed in acetone and left to air dry. Masses were then obtained using a calibrated 5 decimal place balance. The weighed metal was placed into a clean Teflon vial and a precise mass of concentrated nitric acid added to dissolve the metal. The dissolved solution was then transferred to a 500 ml Teflon bottle and additional 3% nitric acid was weighed in to dilute it. The ^{185}Re spike solution was equilibrated with 3 aliquots of each gravimetric solution, which was assumed to have an equivalent composition to NIST SRM 989. Solutions were measured at 200 ppb concentrations and corrected for instrumental mass fractionation as described above for the pure spike solution. The final concentration of the spike solution was obtained by averaging the concentration calculated for each solution analysed. Finally, a dilute ^{185}Re solution was gravimetrically prepared from the concentrated stock. The calibrated isotope ratio, mass fractions and concentration of the spike solution are presented in Table S1.

Table S1: Spike calibration results.

	^{185}Re/^{187}Re	Ratio uncertainty (2 S.D.)	Fraction ^{187}Re	Fraction ^{185}Re	Concentration (µg/g)	Concentration uncertainty (2 S.D.) (µg/g)
Concentrated spike	29.10345	0.14667	0.03322	0.96678	37.731	0.0725
Dilute spike	29.10345	0.14667	0.03322	0.96678	0.01516	0.00011

2. Column calibration

Shrink fit columns with 200µl resin beds were used for the final Re purification step. The final method is described in the manuscript. The method is similar to that presented by Sweere et al. (under review) for the purification of Cd. However, it is adapted here by omitting a HF acid step designed to remove Zn, and instead using 0.4 ml 3M HNO_3 to remove several transition metals (Mo is shown in Fig. S1, but Cd, Zn and others also elute at this stage). Re is finally eluted in 2ml 7.5M HNO_3. Calibration of the method using laboratory standard solutions indicate that the recovery of Re using this method is close to 100% (Fig. S1).

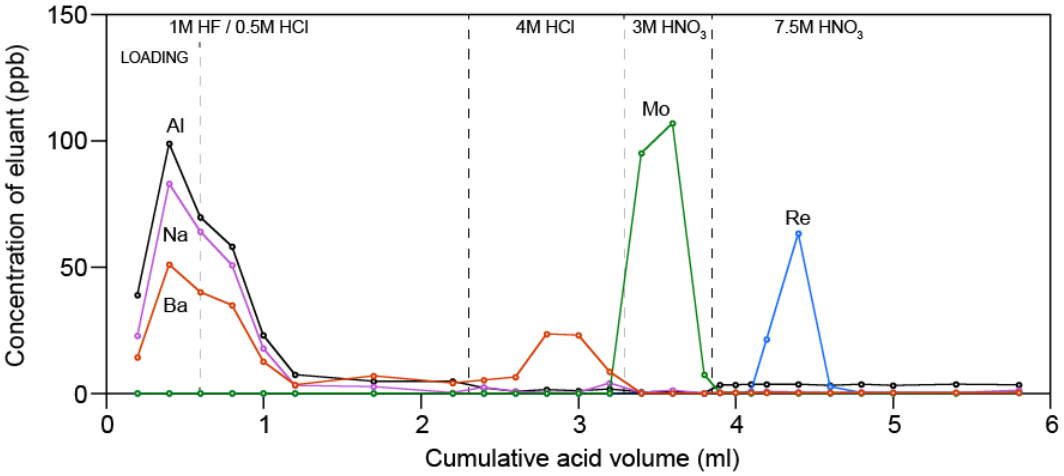

Fig. S2: Calibration of 200µl shrink-fit Teflon columns for Re purification.

3. Data quality

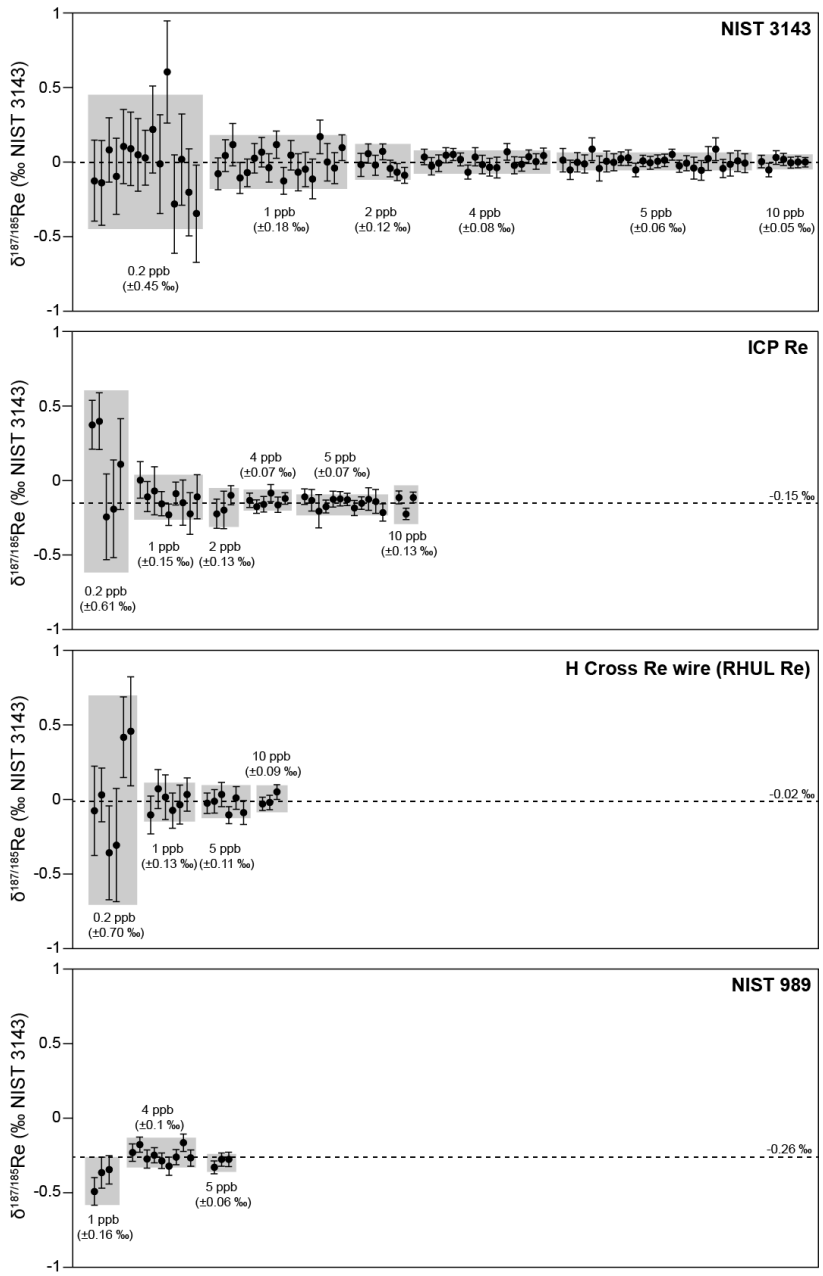

Figure S2: Rhenium solution analyses undertaken on the RHUL Neptune Plus MC-ICP-MS. Details are described in the main manuscript.

References

Gramlich, J.W., Murphy, T.J., Garner, E.L. and Shields, W.R. (1973), Absolute isotopic abundance ratio and atomic weight of a reference sample of rhenium. Journal of Research of the National Bureau of Standards 77A, 691–698.