The rhenium isotope composition of Atlantic Ocean seawater

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Abstract

The concentrations and isotopic compositions of rhenium are presented from seawater samples obtained from the primary station for the Bermuda Atlantic Time Series Study in the North Atlantic Ocean and from the 40°S UK GEOTRACES expedition in the South Atlantic Ocean. Salinity-normalized Re concentrations in both locations range between ~6.8–7.7 ppt between 50–5000 m depth, consistent with previously published concentration data from the North Atlantic and North Pacific Oceans. Rhenium isotope values (expressed as $\delta^{187/185}Re$ relative to NIST 3143) exhibit minimal variation around an average value of -0.17 ± 0.12 ‰ (n = 12, 2 S.D.), irrespective of water depth or water mass. These results confirm that the isotopic composition of perrhenate (ReO_4^-) in seawater is uniform. The new data establish a baseline for evaluating the isotopic mass balance of Re, and for future assessments of whether this global cycle can be disturbed by changes in seafloor redox and/or global weathering rates.

Introduction

The transition metal rhenium is useful for tracing the evolution of Earth's environmental systems over geological time. Rhenium is highly enriched over its typical continental crust concentration of 0.198 pg/g in sedimentary deposits accumulating in reducing settings (Peucker-Ehrenbrink and Jahn, 2001). These high sedimentary enrichments, which are typically the most pronounced of any redox-sensitive element (Brumsack, 2006), have been suggested to occur either due to the reduction of Re(VII) to Re(IV) (Colodner et al., 1993; Chappaz et al., 2008), the thiolation of Re(VII)-S species, or co-precipitation with Fe-Mo-S phases (Helz and Dolor, 2012; Vorlicek et al., 2012) near to the Fe(III)/Fe(II) redox couple (McKay et al., 1997; Morford et al., 2005, 2009).

Rhenium has two isotopes, ^{187}Re and ^{185}Re, which comprise ~63 % and 37 % of natural Re respectively (Gramlich et al., 1973). Net isotopic fractionation (mass dependent and nuclear volume) of up to 1.5 ‰ is predicted to occur between thiolated Re(VII)-S and reduced Re(IV) species, and the perrhenate (ReO_4^-) that is the dominant species of Re in oxygenated seawater, with ReO_4^- having the highest isotopic composition (Miller et al., 2009, 2015). The removal of mass of Re with a lower isotopic composition than seawater into marine sediments accumulating in low-oxygen conditions would have the potential to alter the global seawater isotopic composition if these fluxes changed over geological time. This effect is the basis for the possible application of Re isotopes as a tracer

39   of global ocean redox, in a similar vein to molybdenum, uranium and thallium isotopes, among others

40   (e.g. Stirling et al., 2008; Anderson et al., 2014; Owens et al., 2016; Kendall et al., 2017).

41   Conversely, the isotopic composition of Re in the oceans may also be perturbed by a change

42   in the size or compositions of the input flux. The pre-anthropogenic global riverine Re concentration

43   is ~11.2 pmol/kg (Colodner et al., 1993; Miller et al., 2011), yielding an annual flux to the oceans of

44   ~4.3 x 10^5 mol/yr (Miller et al., 2011). This riverine flux is suggested to be largely controlled by the

45   oxidation of organic carbon and sulfides from terrestrial rocks, as indicated by the close

46   correspondence between dissolved Re and SO_4^{2-} concentrations in rivers globally (Miller et al.,

47   2011), by the close correspondence between Re and organic carbon concentrations in oxidatively

48   weathered soil and shale profiles (Peucker Ehrenbrink and Hannigan, 2000; Hilton et al., 2014), and

49   by the high concentrations of Re associated with n-alkane insoluble organic compounds (Selby et

50   al., 2007). Changes to the locus of Re weathering, from organic-rich to silicate rocks, could thus alter

51   the size and compositions the Re flux to the oceans (Miller et al. 2015; Dellinger et al., 2020).

52   Unfortunately, the development of the Re isotope system as a proxy for either ocean redox

53   or weathering is currently hindered by a lack of data on the various parts of the modern Re cycle:

54   seawater, weathering fluxes, and sedimentary removal fluxes. This paper presents isotopic

55   measurements of dissolved Re in seawater from two vertical profiles in the North and South Atlantic

56   Oceans. These samples span a range of water masses sourced from distinct oceanic regions.

57   Thermodynamic calculations predict that Re should exist in oxygenated seawater as the stable

58   oxyanion perrhenate (ReO_4^-) (Brookins, 1986). The concentration of Re in seawater has previously

59   been determined to fall in the range ~7.29–8.19 pg/g (~39–44 pM), with a relationship with salinity

60   that confirms its generally conservative behaviour (Anbar et al., 1992; Colodner et al., 1993). The

61   intention here is to characterize the isotopic signature of ReO_4^- in seawater; and to test whether this

62   isotope signature is the same in different water masses. These data are an important first step to

63   understanding the global isotopic mass balance of Re, and the processes that might cause this

64   balance to change over geological timescales.

65

66   **Methods**

67   Samples were collected from the UK Geotraces 40°S expedition (GA10) and from the primary station

68   of the Bermuda Atlantic Timeseries Study (BATS). Exact sample positions are noted in Fig. 1.

69   Seawater samples were collected using either a stainless steel (BATS) or titanium (GEOTRACES)

70   rosette, each equipped with 24 Ocean Test Equipment sampling bottles. Seawater was filtered on

71   board into acid-cleaned HDPE containers using 0.2 μm AcroPak^{TM} polyethersulfone filters and

72   acidified immediately with a small amount of distilled HCl to reach pH ~1.7.

73   For Re concentrations, ~20 ml of filtered seawater was weighed directly into a Teflon vial and

74   spiked with a ^{185}Re-enriched spike solution. Vials were sealed and allowed to reflux for 24 hours to

75   achieve spike-sample equilibrium. Subsequently they were evaporated to dryness, refluxed in a 3:1

76   mixture of concentrated HNO_3 and HCl, evaporated again to dryness and re-dissolved in 2 ml 0.2 M

77   HNO$_3$. Re was purified from the seawater matrix using a small anion exchange column. The sample

78   was loaded onto 200 µl clean, pre-conditioned AG1-X8 anion resin (200–400 mesh). Matrix elements

79   were eluted using a further 2 ml 0.2 M HNO$_3$, before Re was eluted with 2 ml 8M HNO$_3$. Two different

80   ^{185}Re spikes were used in the course of this study. For samples processed at the University of

81   Oxford, the DTM (*Department of Terrestrial Magmatism, Washington, USA*) Re spike was used. For

82   samples processed at Royal Holloway, a new spike solution was prepared from metal powder

83   obtained from Oakridge National Laboratories. Full details of the spike calibration procedure and

84   results are described in the supplementary information.

85   For Re isotopes, ~500 ml of water from each sample was evaporated dry in a class 10 laminar

86   flow hood, and re-dissolved in 120 ml 0.25 M HCl. Procedural blanks were spiked with the RHUL

87   ^{185}Re tracer and re-dissolved in the same volume of acid. Re was purified from matrix elements with

88   a two-step column procedure. First, samples were loaded onto pre-cleaned 3 ml AG1-X8 (200–400

89   mesh) anion exchange resin, with a further addition of 10 ml 0.25 M HCl to elute matrix elements.

90   Thereafter, Re was eluted with 28 ml 8M HNO$_3$. In the second step, each sample was evaporated

91   to dryness, re-dissolved in 1 ml 1M HF/0.5M HCl and loaded onto 200 µl anion resin in Teflon

92   columns. Matrix elements were eluted with further additions of 1ml 1M HF/0.5M HCl, 1 ml 4M HCl

93   and 0.4 ml 3M HNO$_3$. Re was eluted with 1.5 ml 8M HNO$_3$. After each Re elution step, resin beads

94   were visible in the Teflon sample vials. To minimize the effect of organic material on mass

95   spectrometry, each sample was dissolved in a small volume of concentrated HNO$_3$ and ultra-pure

96   H$_2$O$_2$ and refluxed for 48 hours at 120°C. They were then evaporated dry and re-dissolved in 0.5 ml

97   3% HNO$_3$. The mass of Re recovered after columns was quantified during concentration check

98   measurement runs by comparing a diluted aliquot of each sample to the signal intensities of external

99   standards.

100   Re isotope ratios were measured in two laboratories. Several of the South Atlantic samples

101   were measured at the University of Oxford using a Nu Instruments MC-ICP-MS attached to an ESI

102   Apex sample introduction system with the spray chamber set to 100°C. This set up was required in

103   order to achieve the requisite sensitivity in wet plasma mode to precisely monitor masses 185 and

104   187. Samples were introduced as 10 ppb solutions to the instrument in 2% HNO$_3$. Each

105   measurement comprised a single block of 30x 10 s integrations, preceded by 10 integrations of blank

106   2% HNO$_3$ to monitor backgrounds. Washout of Re to background levels between samples took ~ 5–

107   10 minutes with 10% HNO$_3$ and 2% HNO$_3$. Backgrounds rose throughout individual analysis

108   sessions to as high as ~1.5% of the total analyte signal, but the measured composition of standards

109   throughout the run did not notably change due to the background signal corrections.

110   Isotope ratios of the BATS samples and replicates of the South Atlantic samples were

111   performed at Royal Holloway using a Neptune Plus MC-ICP-MS fitted with 10^{13} Ω faraday resistors

112   in wet plasma mode, with standard wet-plasma sample cones and 'H' skimmer cones. Samples were

113   introduced to the instrument as 5 ppb solutions using a quartz SIS spray chamber. Each

114   measurement comprised a single block of 40x 8.5 s integrations, preceded by 10 integrations of

115 blank 3% HNO_3. Washout of Re to <0.1 % of the analyte signal was achieved using 3% HNO_3 in ~90

116 s.

117 For both setups, instrumental mass bias was corrected by doping each sample to 30 or 40

118 ppb W with NIST SRM 3163. This method offers a robust correction of the variable matrix

119 contributions in each sample solution, given the similar ionization potentials of Re and W and their

120 linearly related instrumental fractionation factors (Miller et al., 2009; Poirier and Doucelance, 2009;

121 Dellinger et al., 2020). The W/Re ratios employed here (~6–8) were uniform between samples and

122 bracketing standards, and thus do not affect the quality of isotope data via irregular formation of

123 hydrides or peak tailing/abundance sensitivity effects (Dellinger et al., 2020). Measured ratios were

124 corrected for instrumental bias by normalizing to a $^{186}W/^{184}W$ ratio of 0.92767 and applying this to

125 the measured $^{187}Re/^{185}Re$ ratios using an exponential mass bias law (Miller et al., 2009). $\delta^{187/185}Re$

126 values were then calculated relative to bracketing measurements of NIST SRM 3143: $\delta^{187/185}Re =$

127 $[(^{187}Re/^{185}Re_{sample} - {}^{187}Re/^{185}Re_{NIST}) / {}^{187}Re/^{185}Re_{NIST})] * 1000$. The potential interference of ^{187}Os on

128 ^{187}Re was corrected by simultaneously monitoring ^{189}Os during each static measurement. Inter-

129 laboratory accuracy of Re isotope data was monitored through the use of several secondary solution

130 standards: an ICP Re concentration standard, a solution of H Cross company high purity Re wire,

131 NIST SRM 989 and DURH-Re 1. Rhenium isotope ratios of spiked seawater concentration samples

132 were determined from ~250 pg/g solutions by an identical measurement procedure as for isotope

133 ratios, and calculated by isotope dilution from mass-bias corrected $^{185}Re/^{187}Re$ ratios.

134

135 **Results**

136 The isotopic compositions of Re standard solutions are presented in Table 1 and seawater Re

137 concentration and isotopic data are presented in Table 2. Seawater concentrations average 7.23

138 pg/g across the entire dataset. Re isotope compositions are uniform within their uncertainties and

139 average -0.17 ± 0.12 ‰.

140

141 **Discussion**

142 *Data quality and inter-laboratory accuracy*

143 The external reproducibility of Re solution standards improves to <±0.1 ‰ at analyte concentrations

144 >2 ppb, while internal 2 S.E. counting uncertainties improve to <±0.06 ‰ at signal intensities of >~50

145 mV for ^{187}Re (Fig. S2). The low uncertainties at low sample voltages are due to the use of 10^{13} Ω

146 Faraday resistors that increase the signal/noise ratio of small Re beams. For typical measurement

147 concentrations of 4–5 ppb Re, internal errors are approximately ±0.07 ‰, which are comparable to

148 the results of Dellinger et al. (2020) for similar size sample beams using an identical analytical setup.

149 Measurements of secondary solution standards indicate excellent inter-laboratory accuracy

150 (Table 1). The mean $\delta^{187/185}Re$ determined here of NIST SRM 989 relative to NIST SRM 3143, for

151 analyte concentrations >4 ppb, was -0.26 ± 0.1 ‰, which is within uncertainty of the value determined

152 by Miller et al. (2009) of -0.29 ± 0.07 ‰ and the value determined by Dellinger et al. (2020) of -0.28

153 ± 0.04 ‰. Similarly, a solution of high-purity Re wire obtained from H Cross company by Miller et al.
154 (2009) yielded a $\delta^{187/185}$Re of -0.01 ± 0.12 ‰ (re-normalized to NIST 3143); a different aliquot of H
155 Cross Re wire prepared during this study yielded a composition of -0.02 ± 0.1 ‰. Inter-laboratory
156 accuracy is further demonstrated by the similarity in the composition of the DURH-1 Re standard
157 characterized by Dellinger et al. (2020) as 0.16 ± 0.03 ‰, (relative to NIST 3143) and at Royal
158 Holloway in this study (0.13 ± 0.04 ‰). Finally, the mean $\delta^{187/185}$Re values of an in-house ICP Re
159 solution standard analysed at Royal Holloway and Oxford during the course of this study were the
160 same within uncertainties, suggesting that the data produced in both labs is comparable.

161   Procedural blanks, as determined by isotope dilution for concentration and stable isotope
162 measurements, were 4–8 pg, constituting a tiny amount of the total Re processed. Concentration
163 measurements were blank corrected, while isotope measurements were not. Miller et al. (2009), Liu
164 (2015) and Dellinger et al. (2020) showed that ~60% of Re need to be eluted from AG1-X8 resin
165 with 4M HNO_3 to minimize column fractionation to within an uncertainty of ±0.1 ‰ from the 'true'
166 value. Re recoveries in this study were between ~63% and ~100% (Table 2), which are large enough
167 to avoid measurable fractionation. In any case, we used 7.5 M HNO_3 to elute Re: Dellinger et al.
168 (2020) showed that column fractionation effects are negligible when eluting Re with 8M HNO_3.

169

170 *Atlantic seawater Re concentration data*

171 The blank-corrected and salinity-normalized concentrations of the BATS seawater samples
172 measured at RHUL range from 6.79–7.42 pg/g, with an average of 7.16 pg/g. These concentrations
173 are similar to those from the South Atlantic measured in the same lab, which range from 6.86–7.42
174 pg/g (average 7.11 pg/g). The South Atlantic samples measured in Oxford using the DTM ^{185}Re
175 spike have systematically higher concentrations (7.51–7.81 pg/g, average 7.58 pg/g) that are
176 probably due to the precision of the calibrated concentrations of the DTM and RHUL ^{185}Re spike
177 solutions. Two samples (BATS 50 m and BATS 2000 m) were measured at RHUL using four
178 separately spiked aliquots of seawater to assess external reproducibility, accounting for the full
179 chemical separation and measurement procedure. These replicates indicate a precision of ~4–7%
180 on the calculated concentrations. The apparent difference in the seawater concentrations measured
181 on the same samples at RHUL and Oxford is therefore not resolvable outside of the uncertainties.

182   The average concentration of all BATS samples is 7.16 ± 0.34 pg/g (2 S.D.), and the average
183 of the South Atlantic samples is 7.58 ± 0.25 pg/g. The variability in the entire dataset (~5%) is close
184 to that of the sample replicates, thus suggesting that most of the inter-sample variation is related to
185 procedural uncertainties (determination of ^{185}Re/^{187}Re ratios, procedural blanks, spike-sample
186 equilibration) rather than variation within the water column. Concentrations are therefore invariant
187 with depth (Fig. 1). The mean Re concentrations determined in this study are close to the mean
188 concentration of 7.42 ± 0.04 pg/g for North Pacific seawater measured by Anbar et al. (1992) and
189 thus confirm the homogeneity of seawater Re concentrations in different ocean basins.

190

Atlantic seawater $\delta^{187/185}Re$ compositions

192   The isotopic compositions of seawater determined for the BATS samples range from -0.07 ± 0.06

193   ‰ to -0.23 ± 0.06 ‰, and average -0.18 ‰. Excluding one anomalously low replicate (> 2 S.D.

194   deviance from the whole dataset), the average is -0.20 ‰. The Re isotope compositions of the South

195   Atlantic samples range from -0.08 ± 0.06 ‰ to -0.21 ± 0.06 ‰ and average -0.14 ‰. As for the Re

196   concentration data, the BATS and South Atlantic isotope data are therefore not distinguishable

197   outside of the external reproducibility of the method (±0.07 ‰) and are uniform with depth. The data

198   provide constraints on the isotopic composition of several major water masses (North Atlantic Deep

199   Water, Circumpolar Deep Water, Antarctic Intermediate Water, Weddell Sea Deep Water) which

200   exhibit significant differences in water mass chemistry based on traditional nutrient tracers (e.g.

201   phosphate concentrations, Fig. 1) but lack any resolvable differences in $\delta^{187/185}Re$. The lack of depth-

202   dependency in the data is consistent with evidence that Re is not involved in biological processes

203   and therefore not prone to re-mobilisation within the water column during organic matter production

204   and subsequent oxidation (Pilato and Steifel, 1999).

205   The Atlantic seawater Re-isotope composition determined here can be considered

206   representative of the stable perrhenate ion ReO_4^- that constitutes the vast majority of Re in the

207   oceans under typical Eh-pH conditions (Brookins, 1986; Anbar et al., 1992; Colodner et al., 1993;

208   Koide et al., 1995). The close agreement between the $\delta^{187/185}Re$ data from natural samples and the

209    $\delta^{187/185}Re$ composition of the IAPSO seawater standard measured by Dellinger et al. (2020) supports

210   this argument. Additional studies of $\delta^{187/185}Re$ in ocean seawater may yet reveal isotopic differences

211   related to the thiolation, reduction, or sorption of Re under low oxygen or ferruginous conditions, as

212   identified for other dissolved trace metals such as Cd (Janssen et al., 2014; Guinoiseau et al., 2018).

213   *Ab initio* calculations of $\delta^{187/185}Re$ for thiolated and reduced Re species suggest that where such

214   effects are found, they would be liable to produce reaction products with isotopic compositions lower

215   than ReO_4^- (Miller et al., 2015). Nonetheless, it is unclear if such effects would be detectable in the

216   open ocean given the need for reaction products to be removed from seawater on timescales faster

217   than localized ocean mixing. Such effects might be detectable in marginal marine basins where

218   water renewal rates are low, or in stably low oxygen open ocean environments, perhaps above the

219   sediment water interface of upwelling zones.

220

221   *Isotopic mass balance of Re*

222   Determining the $\delta^{187/185}Re$ composition of oceanic ReO_4^- provides a starting point for evaluating the

223   isotopic mass balance of Re in the modern ocean. This task is vital as a first step towards

224   understanding what processes might have perturbed the isotopic system in the geological past.

225   Since *ab-initio* calculations of thiolated and reduced Re species (those likely to be buried in marine

226   sediments) are all isotopically lower than ReO_4^- (Miller et al., 2015), the likely isotopic composition of

227   crustal weathering must also be ≤ -0.17 ‰ for the Re cycle to achieve steady-state. Figure 2 shows

228   predicted compositions of Re weathering fluxes for Re removal into sediments for different

229   proportions of Re(VII)O$_3$S$^-$ (with a composition 0.33 ‰ lower than seawater), Re(IV)Cl$_6^{2-}$ (with a

230   composition 1.52 ‰ lower than seawater) and 'quantitative' Re removal, with no isotopic

231   fractionation from seawater (as observed in the modern ocean for Mo and Zn in euxinic settings).

232   These calculations all indicate an input flux composition that is isotopically lower than seawater, but

233   which could theoretically range anywhere from ~-0.20 ‰ to ~-1.7 ‰.

234   A large proportion of the Re weathered into the oceans is probably sourced from the oxidation

235   of organic matter in sedimentary rocks (Peucker Ehrenbrink and Hannigan, 2000; Hilton et al., 2014).

236   Miller et al. (2015) measured the isotopic composition of Re in samples from a Devonian Shale

237   weathering profile and found that unweathered organic-rich shale had a value of -0.57 ‰

238   (renormalized to NIST 3143). Furthermore, basalt standards analysed by Dellinger et al. (2020)

239   average ~- 0.33 ‰. Both of these studies are consistent with the prediction in Fig. 2 that weathering

240   inputs must have $\delta^{187/185}$Re compositions lower than seawater (-0.17 ‰), but neither they nor the

241   new seawater data can be used to make more precise constraints on this composition. It should also

242   be considered that while Re(VII)-S and Re(IV) species are predicted to have lower $\delta^{187/185}$Re

243   compositions that seawater ReO$_4^-$, the potential for Re to be removed from seawater with a heavy

244   isotopic composition, perhaps by adsorption to organic matter or mineral surfaces, cannot be

245   presently excluded. Lastly, as with all isotope systems, construction of a modern isotopic mass

246   balance for Re proceeds on the assumption that the system is in steady state. However, given the

247   potential for rapid changes in Re weathering and burial over timescales of 10^3 years (e.g. Crusius et

248   al., 1996; Hilton et al., 2014), this condition may not be met in the modern ocean.

249   A significant amount of work is therefore required to establish more precise constraints on

250   the compositions of input and output fluxes of Re to and from the oceans, to allow an improved

251   understanding of how this isotopic system may be utilized to reconstruct oceanic redox and/or

252   weathering processes in the geological past.

253

254   **Conclusions**

255   Re concentration and $\delta^{187/185}$Re data are presented from the BATS primary sampling site in the North

256   Atlantic Ocean and from the GEOTRACES 40°S (GA10) transect in the South Atlantic Ocean.

257   Vertical differences in Re concentrations are not discernable outside of analytical uncertainties and

258   are close to previous estimates of Re concentrations in Pacific seawater. The $\delta^{187/185}$Re of the

259   samples average ~ -0.17 ± 0.12 ‰ and are invariant vertically and with latitude. This value therefore

260   characterizes the Re(VII)O$_4^-$ that constitutes the majority of dissolved Re in the oceans and provides

261   a starting point for evaluating the isotopic mass balance of Re. If sedimentary output fluxes of Re

262   are assumed to have $\delta^{187/185}$Re compositions lower than seawater (Miller et al., 2015), the

263   weathering input flux of Re to the oceans can be predicted to also be < -0.20 ‰. Although a small

264   number of constrains exist on the composition of weathered Re (Miller et al., 2015; Dellinger et al.,

265   2020), more precise estimates of this parameter must await future measurements of Re in rivers,

266   marine sediments and continental crust rocks. A final, important point is that given the unavailability

of Re isotopic standard NIST SRM 989, we suggest that future studies of Re isotopes should use NIST SRM 3143 as a zero-delta reference. The isotopic composition of this solution relative to NIST 989 has now been determined in three different laboratories as +0.29 ‰ (Table 1), and therefore future studies using NIST 3143 will be directly comparable to the pioneering efforts of Miller et al. (2009, 2015) and Dellinger et al. (2020).

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391 **Figures**

392 **Figure 1**: Re concentrations and isotope compositions for (A) the North Atlantic BATS primary site

393 and (B) for the GEOTRACES GA10 40°S transect. The plots to the left of each panel show sample

394 positions superimposed onto water mass dissolved phosphate concentrations extracted from the

395 World Ocean Atlas 2009. Phosphate concentrations are in units of μM. Primary water masses are

396 also displayed. Vertical dashed lines indicate the mean isotopic composition and concentration of all

397 seawater samples analysed. NADW: North Atlantic Deep Water. AABW: Antarctic Bottom Water.

398 SACW: South Atlantic Central Water. SAMW: Sub-Antarctic mode Water. AAIW: Antarctic

399 Intermediate Water. WSDW: Weddell Sea Deep Water.

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401 **Figure 2:** Mass balance model showing the predicted $\delta^{187/185}$Re composition of Re weathered into

402 the ocean. The calculated weathering compositions (dashed lines) assume a steady-state system

403 and different fractional combinations of sedimentary output fluxes of Re as (i) Re(IV)Cl$_6^{2-}$ and

404 Re(VII)O$_3$S$^-$; and (ii) Re(IV)Cl$_6^{2-}$ and 'quantitative' removal of Re into sediments. These removal

405 species/mechanisms were chosen because they cover the largest isotopic range predicted by *ab*

406 *initio* calcuations (Miller et al., 2015), thus yielding the largest possible range of compositions for the

407 input fluxes. Arrows indicate the composition of unweathered shales and basalt standards measured

408 by Miller et al. (2015) and Dellinger et al. (2020) respectively.

409

410 **Tables**

411 **Table 1:** Compilation of standard solutions analysed in this study, Miller et al. (2009) and Dellinger

412 et al. (2020). All $\delta^{187/185}$Re compositions are referenced to NIST 3143 as the zero delta. Uncertainties

413 are the external reproducibilities calculated from several measurements of each solution and are

414 typically slightly larger than the measured internal errors.

415

Standard	Average ± 2 S.D. (‰ rel. to NIST 3143), RHUL	Average ± 2 S.D. (‰ rel. to NIST 3143), OXFORD	Miller et al., Average ± 2 S.D. (‰ rel. to NIST 3143), WHOI	Dellinger et al., Average ± 2 S.D. (‰ rel. to NIST 3143), DURHAM
NIST 3143	0 ± 0.08	0 ± 0.08	0	-
NIST 989	-0.27 ± 0.10 (n = 14)	-	-0.29 ± 0.07	-0.28 ± 0.04
ICP Re	-0.15 ± 0.07 (n = 21)	-0.19 ± 0.09 (n = 13)	-	-
H Cross Re wire	-0.02 ± 0.10 (n = 9)	-	-0.01 ± 0.12	-
DURH-Re 1	0.14 ± 0.03 (n = 3)	-	-	0.16 ± 0.03

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417

418 **Table 2:** BATS data.

Sample	Salinity (PSU)	Re concentration (pg/g)	$\delta^{187/185}$Re (‰ NIST 3143)	2 S.E.	% Recovery
50 m	36.61	7.01			
50 m	36.61	7.36			
50 m	36.61	6.79			
50 m	36.61	6.94			
200 m	36.58	7.40	-0.22	0.10	63
200 m	36.58	6.86			
400 m	36.50	7.18	-0.23	0.06	82
800 m	35.29	7.11	-0.21	0.06	108
800 m	35.29	7.20			
1000 m	35.09	7.10	-0.19	0.06	107
1000 m	35.09	7.06			
2000 m	34.97	7.31			
2000 m	34.97	7.03			
2000 m	34.97	7.42			
2000 m	34.97	7.11			
3000 m	34.92	7.27	-0.25	0.09	85
3000 m	34.92	7.38	-0.07	0.06	72
4500 m	34.88	7.13	-0.21	0.06	88
4500 m	34.88	7.41			

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422 **Table 3:** 40ºS GEOTRACES GA10 data. Samples marked with an asterisk are from Oxford. All other
423 samples were analysed at RHUL.

GEOTRACES Bottle code	Water depth (m)	Salinity (PSU)	Re concentration (pg/g)	$\delta^{187/185}$Re (‰ NIST 3143)	2 S.E.	% Recovery
0179	51	34.88	6.96			
0179	51	34.88	7.21			
2327	58	36.72	7.09	-0.21	0.06	98
1550	97	35.26	6.86			
1550	97	35.26	7.17			
1550*	97	35.26	7.55			
2006	496	34.18	7.02			
2006	496	34.18	7.42			
2006*	496	34.18	7.81	-0.19	0.14	70
2006*	496	34.18		-0.08	0.10	72
2279*	1492	34.47	7.56			
2276*	1988	34.80	7.51	-0.08	0.06	76
2269*	2985	34.75	7.54			
1952*	5103	34.67	7.67	-0.14	0.15	81

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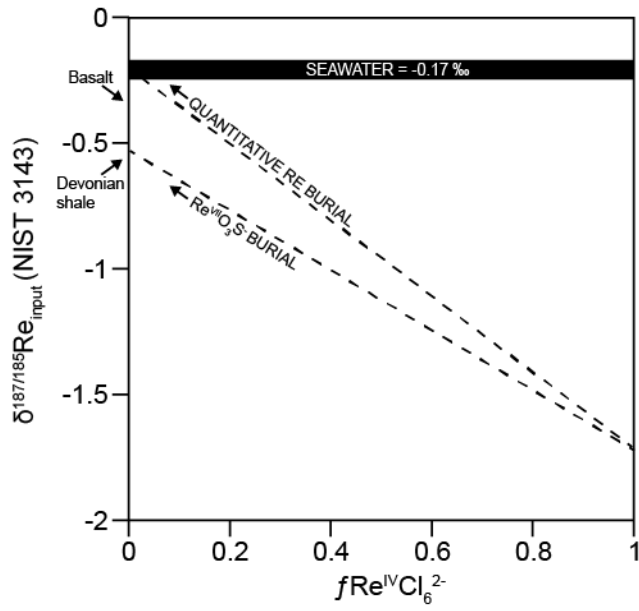432

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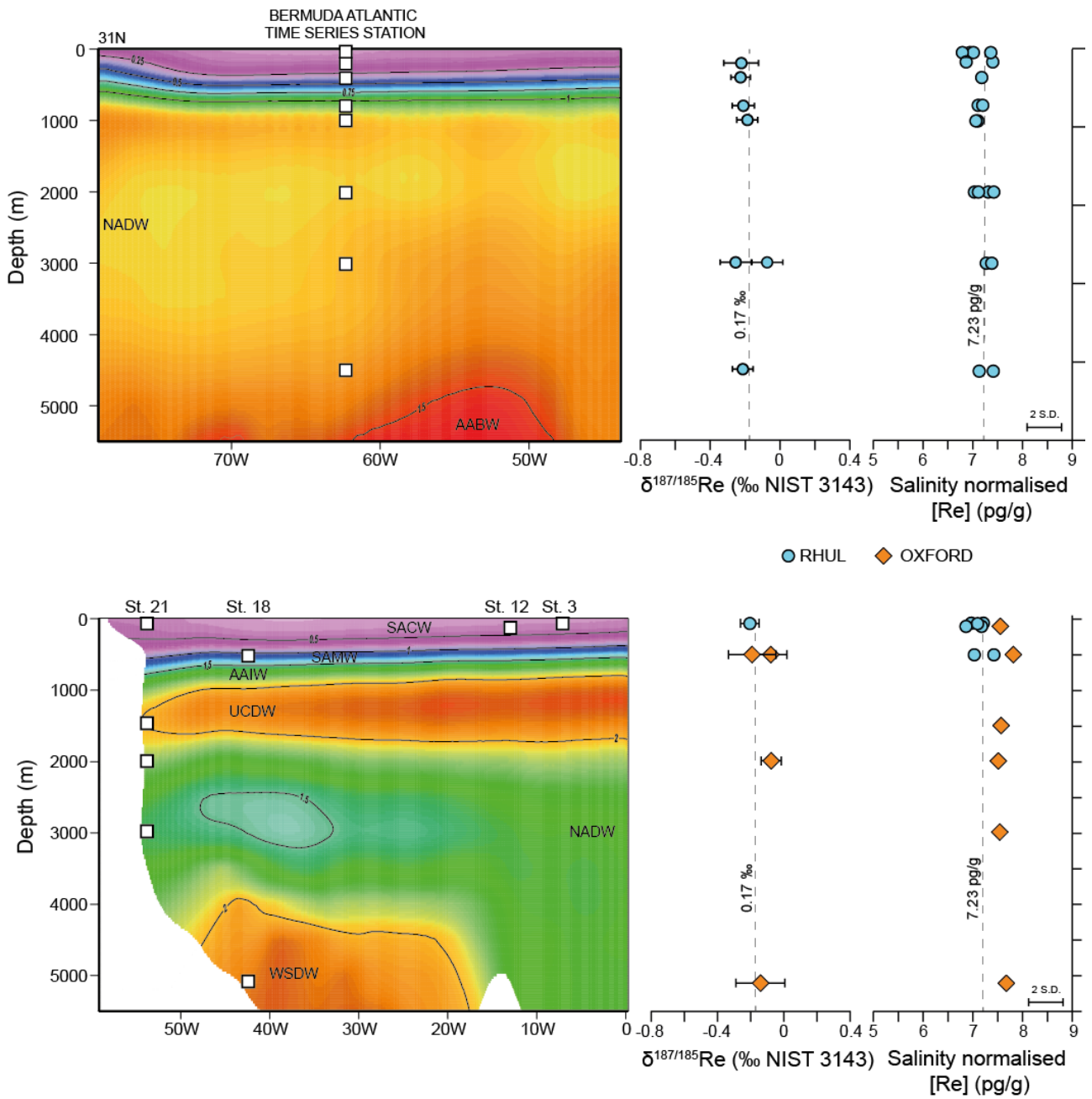
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445   Figure 2

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