

Rhenium measurements on North Atlantic seaweed samples by ID-ICP-MS: An observation on the Re concentration factors

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The estimation of the Re concentration factor (CF) has been carried out to provide additional field information on the biochemical similarities between Re and Tc. Re concentration in brown seaweed samples from the North Atlantic Coast were measured using ID-ICP-MS. The chemical yields were quantitative, and the concentrations were distributed within a narrow range of 65–80 ng/g d.w. CF of Re was approximately $1.2 \cdot 10^4$ on average, i.e., one order of magnitude less than that found for ⁹⁹Tc.

Introduction

Rhenium is a very interesting element from a geochemical viewpoint due to its sensitivity to redox potentials. However, Re is one of the most scarce natural elements on the earth's surface, and its determination in geological and environmentally relevant samples has been extremely difficult. The determination traditionally required the use of neutron activation analysis (NAA) technique,^{1,2} and many analyzed concentrations were near the detection limits. The recent development of accurate mass spectrometry techniques such as ICP-MS, has allowed researchers to expand the knowledge about the geochemical behavior of this element.^{3,4}

Attention has been put on Re during the last few decades, because it is expected to show a high similarity between its environmental behavior and that of the fission product ⁹⁹Tc based on its Eh–pH diagram.⁵ Additionally, it is expected that ⁹⁹Tc will become a very important contributor to the doses received by the future general population based on its long half-life ($T_{1/2} = 2.1 \cdot 10^5$ y) and its high mobility under oxic environment. However, the environmental concentrations of ⁹⁹Tc are usually very small, and its low energy beta-emission ($E_{avg} = 242$ keV) makes the quantification difficult in environmental samples using radiometric techniques.

The chemical similarities between the behavior of Re and Tc have been proved by laboratory tests. Rhenium has been proposed as a Tc chemical analogue a tracer for Tc in radiochemical recovery calculations, using both radiometric⁶ and non-radiometric⁷ methods. Thus, it was suggested that predictions on the Tc environmental geochemistry could be done using the results found for Re.³ This strategy would offer researchers the following advantages: (1) Re is a natural element with well defined isotopic ratios, unlike Tc which is a radioactive artificial element and (2) Re concentrations in the nature are

significantly larger than those of Tc. Both circumstances seem to indicate Re can be studied easier than Tc in the natural environment.

However, there is a certain lack of knowledge regarding the behavior of Re in the nature. For example, transfer factors (TF) or concentration factors (CF) of Tc for different vegetable species have been calculated using both laboratory experiments⁸ and field measurements,⁹ but there are no systematic calculations for Re CFs in the literature. Strong efforts are being made to address this lack.

Any hypothesis on differences and similarities between the respective geochemistries of Re and Tc must be supported using field data. From this viewpoint, brown seaweeds are among the most interesting vegetable species to be checked. It is well known that Tc is highly concentrated by brown seaweeds.¹⁰ Due to the very conservative behavior of Tc as TcO_4^- ion in the environment, brown seaweed can be used (and they actually are being used)¹⁰ as bioindicators for Tc concentration in seawater. Therefore, checking the rhenium concentration capacity of brown seaweeds could support or negate the possibility of using Re as a stable analogue for Tc in order to understand the chemical behavior of Tc in the environment.

In this work, we describe a preliminary estimation of the concentration factor of Re in brown seaweed samples taken from the North Atlantic Ocean. They were analyzed for Re contents using isotope dilution (ID) – inductively coupled plasma mass spectrometry (ICP-MS) after a chemical separation scheme designed in order to remove impurities from the sample which could produce severe interferences in the spectra. Unfortunately, there were no seawater samples available, and therefore, the direct measurement of Re in seawater was not possible. However, Re concentration in seawater is fairly uniform¹¹ so that we used a published value for seawater in our analysis. We compared our Re CFs to the reported Tc CFs.

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Experimental

Samples and chemicals

Five samples of brown algae (*Fucus vesiculosus*) were taken on the coast of Utsira, southwest of Norway, in the year 2000 on a monthly basis. Dates of collection are provided in Table 1. Samples were periodically taken in the framework of an evaluation program of environmental radioactivity in Nordic waters.¹² Five replicates of every sample were analyzed to compare the results obtained in this work for Re and Tc chemical yields.

After collection, the seaweed samples were thoroughly dried, and sediment particles were removed by shaking. The samples were homogenized using a mechanical sample homogenizer. Then, they were transferred to cylindrical PEEK beakers, and sealed for transport to the laboratory.

Nitric acid used was ultrapure-analytical grade (Tama AA-100; Tama Chemicals Co., Ltd, Kanagawa, Japan). Deionized water (>18 M Ω) was obtained from a Milli-Q water system (Nihon Millipore K.K, Tokyo, Japan). Prepacked columns of Tc-selective chromatographic resin (TEVA, Eichrom Industries, Inc., Sowa Trading Company, Inc., Tokyo, Japan) were used for the separation of Tc and Re. The high selectivity of this resin for ReO₄⁻ and TcO₄⁻ has already been reported.^{13,14}

Enriched ¹⁸⁵Re (chemical form: ReO₄⁻) was used as chemical yield carrier for Re. The ¹⁸⁵Re isotope enriched solution was produced by dissolving a suitable amount of the solid supplied by the Oak Ridge National Laboratory, TN, USA (96.74±0.01% isotopic abundance of ¹⁸⁵Re) to 6M HNO₃. In this way, the Re chemical yield can be calculated using the ID method, as Re natural abundances are 37.40% (¹⁸⁵Re) and 62.60% (¹⁸⁷Re).

Method of the analysis

Both the sample pretreatment and the whole separation method have been published elsewhere,¹⁵ and, therefore, only a short summary is described here.

A 0.5-g amount of each sample was spiked with 35 ng of ¹⁸⁵Re-enriched solution. Then the samples were subsequently reduced to ashes. The residues were dissolved by leaching with 8M HNO₃ and the filtrate was conditioned to 0.1M HNO₃. The TEVA·Spec™ chromatographic resin was used to concentrate Re. Interfering W was removed using 20 ml of 1M HNO₃. Re was stripped from the resin using 5 ml of 8M HNO₃. Previous studies^{14,15} have shown the high efficiency of this stripping process. Finally, the solution was adjusted using deionized water to get a 0.1M HNO₃ solution.

Table 1. Collection dates of the seaweed samples

Sample	Date of collection
3014	2000/01/11
3015	2000/02/11
3016	2000/03/13
3017	2000/04/13
3021	2000/08/16

Both the chemical yield and concentration for Re were calculated using the isotope dilution method with the ICP-MS (Agilent-7500 Yokogawa, Japan). The calculations for Re recovery and concentration are based on isotopic ratios, and therefore an internal standard is not necessary.

It is possible to generate Re isobars by forming hydrides with W isotopes at masses 185 and 187. The developed method was checked for the potential to generate isobars in each measurement. To do that, a stable W isotope at mass 182 was monitored in each sample replicate. The concentration of W in every sample was in the range of 0.1–70 pg/ml. Hence, no interference in the mass spectra of Re is expected.

Results and discussion

The chemical yield and rhenium concentration for each sample replicate are listed in Table 2. These results showed relatively good homogeneity for every sample, although, there were some exceptions. The fourth replicate of sample 3021 produced a chemical yield larger than 100%, however, this result should be actually covering a chemical yield of 100% within a 1 σ uncertainty interval. Both the anomalous result and very large uncertainty were due to plasma condition fluctuations during the ICP-MS analysis. The chemical yields were quantitative (i.e., >80%) showing the high efficiency of the separation method.

All the concentrations were in a very narrow range (65–85 ng/g). An average value could be easily calculated after minimizing the resulted χ^2 distribution:

$$\chi^2 = \sum_{i=1}^{25} \left(\frac{x_e - x_i}{\sigma_i} \right)^2$$

where x_e is the estimated value of the Re concentration, x_i are the values obtained for each of the sample aliquots and σ_i are their respective uncertainties. By minimizing this expression it is easy to see that:

$$x_e = \frac{\sum_{i=1}^{25} \frac{x_i}{\sigma_i^2}}{\sum_{i=1}^{25} \frac{1}{\sigma_i^2}}$$

and its corresponding uncertainty is:

$$\sigma = \sqrt{\frac{1}{\sum_{i=1}^{25} \frac{1}{\sigma_i^2}}}$$

In this way, an average concentration of 74.5 ± 0.9 ng/g d.w. was obtained. Comparisons were made with published concentrations. Different species of brown seaweed from the American Pacific Ocean were analyzed for Re,¹⁶ and the concentrations were within a range 7–22 times less than the values reported here. Our values for the green algae *Bryopsis maxima* were 72 times less than the concentrations reported by ISHII et al.¹⁷ As expected, this meant that only a comparison for the same species of seaweed could be representative, and, possibly, similar age populations must be compared.

To the best of our knowledge, the only recently published data on this subject estimated the Re concentration in a *Fucus* sample collected in the Ireland Sea to be about 20 ng/g.¹⁸ This value was 3–4 times less than our results, despite the facts that the seaweed species were the same. Accordingly, the available mechanisms for Re intake should be the same. Furthermore, if the Re concentration in Atlantic seawater could be assumed to be relatively uniform, the Re concentration in the seaweed samples should be approximately the same.

Table 2. Re chemical yields and concentration values for the samples

Sample and replicate	Re recovery, %	Re concentration, ng/g d.w.
3014	79.0 ± 3.3	84.9 ± 5.9
	98.0 ± 3.3	82.6 ± 4.6
	93.2 ± 3.6	79.6 ± 5.0
	98.0 ± 3.9	84.4 ± 5.4
	96 ± 11	79.7 ± 15.8
3015	95.6 ± 3.6	78.6 ± 4.8
	90.3 ± 3.2	73.4 ± 4.4
	99.5 ± 2.7	67.7 ± 2.5
	99.1 ± 3.8	72.8 ± 4.9
	93.3 ± 3.7	76.7 ± 5.4
3016	80.2 ± 2.6	75.6 ± 3.9
	98.3 ± 4.4	82.1 ± 6.1
	102.6 ± 3.3	77.6 ± 3.8
	96.3 ± 3.3	79.6 ± 4.5
	92.2 ± 3.2	76.3 ± 4.5
3017	84.7 ± 2.4	77.1 ± 3.3
	99.3 ± 3.3	80.0 ± 4.5
	92.0 ± 3.3	78.1 ± 4.8
	97.1 ± 2.9	79.5 ± 3.7
	91.5 ± 3.9	82.6 ± 5.6
3021	100.2 ± 3.0	68.6 ± 3.2
	95.6 ± 3.7	70.3 ± 4.6
	95.1 ± 4.1	60.8 ± 4.4
	110 ± 14	63.2 ± 14.8
	92.7 ± 3.6	62.7 ± 3.7

Unfortunately, Re concentration in seaweed samples was not the major objective for MCCARTHY et al.,¹⁸ hence, no analytical details or further discussion on this subject are available. We considered and rejected several possible explanations for such concentration differences.

(1) Those differences could be related to the age of the seaweed itself, i.e., the total time elapsed along the seaweed life span to collection date. *Fucus* is a perennial seaweed genre which has a life span of several years.¹⁹ If a very young seaweed specimen were collected, Re accumulation could reasonably be different than that found in an older specimen. Such differences should be reflected in the Re concentrations. However, according to the laboratory experiments of YANG,¹⁶ the Re intake to brown seaweed seemed to be a very fast process, taking less than two hours for its accumulation to reach an equilibrium value. If these findings could be extrapolated to our experiment, there would not be any effect related to the seaweed age.

(2) Another consideration could be whether the Re content of seawater are the same at different locations (i.e., the Irish Sea and the southwestern coast of Norway). The possibility of different concentrations could not be easily understood. The Re concentrations in Atlantic Ocean seawater have been reported as ranging from 4.0 to 6.9 pg/g.¹¹ However, those differences did not seem to justify the differences between our results and those in MCCARTNEY et al.¹⁸ Re concentration factors in *Fucus sp.* should be the same at both locations, therefore, a difference for Re concentrations in seawater by a factor of 3–4 would be necessary. However, it is expected that these concentrations were homogeneous throughout North Atlantic Ocean.

(3) Another consideration would be whether the concentration capacity of *Fucus* seaweed throughout the year would remain constant or not. Seasonal variations could be related to changes in seawater conditions, and, therefore, the intake and excretion mechanisms could eventually be enhanced or depressed according to factors such as water depth (i.e., sunlight transference to the seaweed location), salinity, etc. Indeed, there are recent reports on variations of stable iodine concentration through one order of magnitude in *Fucus vesiculosus* samples collected from the same region as our samples.²⁰ Such variations are probably due to the seasonal variation of seaweed and different growth parts of seaweed.²¹

A possible explanation could be related to the seawater conditions at both locations (i.e., the Irish Sea and the Atlantic off Norway). Re is expected to appear in the form of ReO_4^- under oxic conditions. However, chemical availability for biota and sediment particles could change according to the seawater conditions, as it has been shown for Tc.²² It should be questioned if the Re bioavailability could change accordingly. If seawater conditions differ from one sampling location to another

one, it could be said that Re bioavailability (and its corresponding seaweed concentration) differed, but in a similar way.

It is very interesting to note that all the 3021 sample replicates resulted in Re concentrations systematically lower than those found for the rest of the sample set (approximately by 10–15%). We cannot provide an explanation for this finding. Possibly, the previous discussion regarding the differences of Re concentrations in brown seaweed could be applied here.

There is another point to be established as a base for further research. The average Re concentration in Atlantic seawater has been estimated as approximately 6.5 pg/g.¹¹ This result allows a rough calculation for the Re concentration factor of the *Fucus vesiculosus* seaweed. Taking the average Re concentration calculated from Table 2, we find an average CF value of approximately $1.2 \cdot 10^4$. It is interesting to see that this value is 10 times less than the CF calculated for Tc¹⁰ for this seaweed species, despite geochemical similarities between both elements.

The explanation for this result could be related to the previously suggested facts on influences for the uptake and excretion of Re by the seaweed. It is known that Tc arrives in the seaweed environment in successive tides according to the release rate from the major nuclear fuel reprocessing plants at Cap La Hague (France) and, especially, Sellafield (UK), with a well defined residence time. By contrast, it would be expected that Re would be available in a continuous way, and not arriving with successive tides. As a consequence, reaching equilibrium between the different compartments (i.e., seawater and seaweed) could follow different regimes, affecting the corresponding concentration capacities.

A comparison could be established among our results and several seaweed field CF values for Tc and Re published in the literature,^{1,16,17,23,24} a summary can be found in Table 3. Only Re values were included, and then Tc CF values only when available for the same

species or another one from the same genre. This is the case for *Laminaria sp.*, for *Laminaria digitata*, Tc CF was evaluated, but Re CF was not, and Re CF has been evaluated for *Laminaria sinclarii*, but not Tc CF.

There are only two species in which accumulation capacities for Re and Tc have been previously evaluated, *Enteromorpha* and *Fucus Disticus*; they are a green and a brown algae, respectively. It is easy to see that for both of them the CF values for Re are less than those for Tc by approximately 1 up to 2 orders of magnitude. This fact agreed well with our results. Indeed, the value estimated here is within the range of CF values previously determined, and it is within the larger values. It is interesting to see that, besides the differences in 1–2 orders of magnitude, the qualitative nature of our results is in agreement with previous observations done for Tc, i.e., *Fucus sp.* has one of the highest CF values (for both Tc and Re) in brown seaweed.

These interesting results should encourage research to be continued on these topics. Systematic studies on the Re distribution over different ecosystems must be done in order to allow comparison of its geochemical behavior with that of its artificial analogue, Tc.

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Table 3. A summary of literature CF values for Re and Tc in several seaweed species and the present results

Seaweed species	Tc CF, l/kg d.w.	Re CF, ml/g d.w.
<i>Bryopsis Maxima</i>		$7.4 \cdot 10^5$
<i>Chaetomorfa sp.</i>		66
<i>Codium fragile</i>		121
<i>Enteromorpha</i>	428	66
<i>Fucus disticus</i>	$1.1 \cdot 10$	$1.1 \cdot 10^3$
<i>Fucus vesiculosus</i>	$7.1 \cdot 10^4 - 1.8 \cdot 10^5$	$1.2 \cdot 10^4$
<i>Fucus serrata</i>	$5.0 \cdot 10^4 - 1.2 \cdot 10^5$	
<i>Laminaria digitata</i>	$2.4 \cdot 10^5$	
<i>Laminaria sinclarii</i>		$4.5 \cdot 10^2$
<i>Pachydictyon coriaceum</i>		$4.4 \cdot 10^2$
<i>Pelvetia carnaliculata</i>	$7.6 \cdot 10^4 - 1.1 \cdot 10^5$	
<i>Pelvetia fastigiata</i>		$1.2 \cdot 10^3$
<i>Ulva sp.</i>		$1.5 \cdot 10^3 - 2.2 \cdot 10^3$

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