Elsevier Editorial System(tm) for Geochimica et Cosmochimica Acta
Manuscript Draft

Manuscript Number: GCA-D-16-00273R1

Title: Osmium uptake, distribution and $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ composition in Phaephyceae macroalgae, Fucus vesiculosus: implications for determining the Os isotope composition of seawater

Article Type: Article

Corresponding Author: Miss. Blanca Racionero Gómez,

Corresponding Author's Institution: Durham University

First Author: Blanca Racionero Gómez

Order of Authors: Blanca Racionero Gómez; Adam D Sproson; David Selby; Darren R Gröcke; Chris H Greenwell; Mouchine Gannoun; Kevin Burton

Abstract: The osmium isotopic composition ($^{187}Os/^{188}Os$) of seawater reflects the balance of input from mantle-, continental- and anthropogenic-derived sources. This study utilizes the Phaeophyceae, Fucus vesiculosus, to analyse its Os abundance and uptake, as well as to assess if macroalgae records the Os isotope composition of the seawater in which it lives. The data demonstrates that Os is not located in one specific biological structure within macroalgae, but is found throughout the organism. Osmium uptake was measured by culturing F. vesiculosus non-fertile tips with different concentrations of Os with a known $^{187}Os/^{188}Os$ composition (~0.16), which is significantly different from the background isotopic composition of local seawater (~0.94). The Os abundance of cultured non-fertile tips show a positive correlation to the concentration of the Os doped seawater. Moreover, the $^{187}Os/^{188}Os$ composition of the seaweed equaled that of the culture medium, stongly confirming the possible use of macroalgae as a biological proxy for the Os isotopic composition of the seawater.

Osmium uptake, distribution, and ^{187}Os/^{188}Os and ^{187}Re/^{188}Os compositions in Phaeophyceae macroalgae, *Fucus vesiculosus*: Implications for determining the ^{187}Os/^{188}Os composition of seawater

B. Racionero-Gómez,[1], A. D. Sproson[1], D. Selby[1], A. Gannoun[2], D. R. Gröcke[1], H. C. Greenwell[1], K, W. Burton[1]

[1]Department of Earth Sciences, Durham University, Durham, DH1 3LE, UK
[2]Campus Universitaire des Cézeaux, 6 Avenue Blaise Pascal TSA 60026 - CS 60026, 63178 AUBIERE Cedex, France

Correspondence to: B. Racionero Gómez (blancaraci@gmail.com telephone: +34646976656) and D. Selby (david.selby@durham.ac.uk telephone: +441913342294 fax: +44 0191 3342301)

Abstract

The osmium isotopic composition ($^{187}Os/^{188}Os$) of seawater reflects the balance of input from mantle-, continental- and anthropogenic-derived sources. This study utilizes the Phaeophyceae, *Fucus vesiculosus,* to analyse its Os abundance and uptake, as well as to assess if macroalgae records the Os isotope composition of the seawater in which it lives. The data demonstrates that Os is not located in one specific biological structure within macroalgae, but is found throughout the organism. Osmium uptake was measured by culturing *F. vesiculosus* non-fertile tips with different concentrations of Os with a known $^{187}Os/^{188}Os$ composition (~0.16), which is significantly different from the background isotopic composition of local seawater (~0.94). The Os abundance of cultured non-fertile tips show a positive correlation to the concentration of the Os doped seawater. Moreover, the $^{187}Os/^{188}Os$ composition of the seaweed equaled that of the culture medium, stongly confirming the possible use of macroalgae as a biological proxy for the Os isotopic composition of the seawater.

Keywords

Osmium, macroalgae, rhenium, isotope composition, seawater, *Fucus vesiculosus*

1. Introduction

Osmium (Os) is one of the least abundant elements in seawater, with a concentration in the open ocean of ~0.01 ppt (Chen and Sharma, 2009; Gannoun and Burton, 2014; Levasseur et al, 1998; Sharma et al, 1997), which is significantly lower than the average crustal abundance (30 - 50 ppt; Peucker-Ehrenbrink and Jahn, 2001; Wedepohl, 1995). Thermodynamic data predict that Os in seawater likely exists as the species OsO_4^0, $HOsO_5^-$ and $H_3OsO_6^-$ (Palmer et al., 1988; Yamashita et al., 2007), with all speciated forms present in the highest oxidation state available to Os. However, chloride complexing is also possible ($OsCl_6^-$, Cotton and Wilkinson, 1988), and it has also been suggested that Os exists as an organo-complex (Levasseur et al., 1998). Osmium in seawater has been shown to exhibit both conservative and non-conservative behaviour (Chen and Sharma, 2009; Gannoun and Burton, 2014), with the present day seawater Os isotope ($^{187}Os/^{188}Os$) composition inferred to reflect Earth surface processes, i.e. the balance of inputs from radiogenic continental-derived and unradiogenic mantle-derived sources (Peucker-Ehrenbrik and Ravizza, 2000; Cohen et al., 2003; Banner, 2004).

Brown macroalgae (i.e. seaweed) are known to concentrate many metal cations and metal oxoanions in a variety of complexes with biopolymers, e.g. alginate, proteins, polysaccharides of the cell wall, fucans, etc. (Davis et al., 2003). To date, positively charged metals associated with macroalgae have been extensively studied (e.g., Ragan et al., 1979; Chapman and Chapman, 1980; Karez et al., 1994; Lobban and Harrison, 1994; Raize et al., 2004). However, relatively little is known about the mechanisms by which macroalgae uptake negatively charged metal oxoanions. To our knowledge, there have been no studies discussing the uptake amount and accumulation of Os by any macroalgae species, although it is known that Os, in addition to Re can accummulate in seaweed (Scadden et al, 1969; Yang, 1991; Mas et al., 2005; Prouty et al., 2014; Racionero-Gómez et al, 2016; Rooney et al, 2016). The brown macroalgae (Phaeophyceae) *Fucus vesiculosus* is observed to be one of the greatest accumulators of metals (Scadden et al, 1969; Morries and Bale, 1975; Bryan, 1983; Yang, 1991; Rainbow and Phillips, 1993; Karez et al., 1994; Mas et al., 2005; Racionero-Gómez et al., 2016).

As such, this study investigates *F. vesiculosus* to establish both the specific sites and the mechanisms of Os accumulation. We also evaluate the importance of macroalgae in recording the direct Os isotope composition of seawater. Here we present the Os abundance for different structures of *F. vesiculosus*: holdfast, stipe, tips, vesicles and blades (Fig. 1) and we determine the uptake rate of Os in macroalgae via cultures of *F. vesiculosus* under different Os concentrations. We also demonstrate experimentally that macroalgae records the Os isotope composition of the local environment in which it lives (i.e. seawater), indicating that seaweed has the ability to record the interaction between the ocean and the Earth's surface, a mechanism proposed for brown algae based on samples collected from the west coast of Greenland and the Gulf of Mexico (Rooney et al, 2016). In addition, we present the rhenium (Re) abundance, and the ^{187}Re/^{188}Os composition of the macroalgae studied.

2. Material and methods

2.1 Macroalgae used in this study: *Fucus vesiculosus*

F. vesiculosus is a common brown macroalgae found along sheltered shores of the North Sea, Baltic Sea, Atlantic Ocean and Pacific Ocean. *F. vesiculosus* produces air bladders annually allowing the individual fronds to float in the upper portion of the water column to permit photosynthesis. The species comprises an anchoring holdfast and a frond made up of a stipe, blades, tips and vesicles (Fig. 1). The growth rate of *F. vesiculosus* ranges between 0.05–0.14 cm/day (Carlson, 1991; Strömgren, 1977), with the species having a life span between 3 to 5 years (White, 2008). The species is annually episodic, gonochoristic and highly fecund (i.e. prolific; White, 2008). *F. vesiculosus* has both fertile tips and non-fertile tips. Fertile tips contain receptacles from which the gametes are released to the seawater and the eggs are fertilized externally. The zygote then starts to develop as soon as it settles into a substrate (Graham and Wilcox, 2000). Non-fertile tips are composed of a parenchymatous thallus i.e. tissue like structure (Graham and Wilcox, 2000; Hiscock, 1991; White, 2008).

The *F. vesiculosus* samples were collected from within the harbour at Staithes and adjacent to the eastern (seaward) side of the east harbour wall, North Yorkshire, UK (Fig. 2) in May, 2014 and June, 2015 (Fig. 2). The Lower Pliensbachian Staithes Sandstone Formation (a 30m thick argillaceous silty sandstone interbedded with 2 to 4 m thick sequences of fine-grained laminated sandstone) comprises the geology of the harbour, beach and village of Staithes, with the cliffs to the east of the harbour coinsisting of the Upper Pliensbachian Cleveland Ironstone Formation (dark argillaceous siltstone and silty sandstone with oodial ironstone; Rawson and Wright, 2000). The May 2014 *F. vesiculosus* collection (Five *F. vesiculosus* specimens held on the same rock) were taken from the eastern side of the east harbour wall (54°33'32.5"N 00°47'15.5"W; Fig. 2). These *F. vesiculosus* samples were utilised to determine the Os abundance of specific structures of the macroalgae. Additional *F. vesiculosus* samples collected in June 2015 were taken from a single location to avoid genetic variation from the mouth of Staithes Beck within the harbour of Staithes (54°33'32.8"N 00°47'25.5"W; Fig. 2). The non-fertile tips (~100) of the June 2015 sample collection were utilised for culture experiments. Seawater used in the culture experiments was taken from the same location as the June 2015 *F. vesiculosus* sample set. An aliquot of the collected seawater was utilised for Re-Os abundance and isotope composition determination.

2.2 Sample preparation and culturing

Prior to analysis all collected specimens were kept individually in plastic sample bags for transport, and stored in a freezer (-10 ºC) for 48 h. Each specimen was washed and rinsed in deionised (Milli-Q™) water to remove any attached sediment and salt. To establish the abundance and distribution of Os in the macroalgae the sample was divided into different structural components: fertile tips, non-fertile tips, vesicles, stipe, holdfast, and blades (Fig. 1). In addition, a mixture of the above components was created to determine an average Os abundance of the whole macroalgae structure. Each structure was dried in an oven at 60 ºC for 12 hrs, prior to powdering to a powder in an agate pestle and a mortar.

In addition, to investigate the uptake of Os by macroalgae, culture experiments were conducted in seawater (modified after Gustow et al. (2014)) in the School of Biological and Biomedical Sciences at Durham University. In total, three separate culture experiments were conducted, with each experiment replicated a total of three times. For each experiment, non-reproductive apical thallus tips were taken from separate *F. vesiculosus* June 2015 specimens of the geographical area (length ≥1.5 cm; wet weight (WW) = 0.12–0.15 g) without visible microalgae (i.e. epiphytes). The apical thallus tips were placed into a 250 mL glass jars containing two plastic mesh shelves. Three tips were placed in the bottom of the jar and three tips were placed in each mesh, having in total nine tips of different specimens in each jar (see Fig. 3). All culture experiments were carried out using filtered (0.7 μm) seawater from Staithes, North Yorkshire, UK (54°33'32.8"N 00°47'25.5"W; Fig. 2) collected in June 2015. The seawater was collected and stored in cleaned PFA Teflon bottles (following the method of Sharma et al., 2012). The source of Os used to dope the natural seawater for the culture experiments is DROsS (Durham Romil Osmium Standard; Nowell et al., 2008). DROsS is an in-house Os solution reference material that possesses a $^{187}Os/^{188}Os$ composition of 0.160924 ± 04 (2SD; Nowell et al., 2008). The DROsS solution utilized in this study is in chloride form. The Re and Os abundance and isotope composition of the collected seawater at Staithes was also determined as part of this study (see methodology below).

To reduce evaporation while to allowing gaseous exchange with the atmosphere all the jars were loosely sealed. No nutrients were added to the Os doped seawater culture solution. The jars, plus tips, were placed into an incubator with a set light/dark rhythm of 16:8, light intensity of 125 μmol photons/$m^2 \cdot s^2$ and a temperature of 11 ºC. The wet weight (WW) of the algal tips in each jar was measured every 2–3 days during the 14 day culturing period. At the same time, the seawater Os-doped culture medium was changed (5 times in total) to avoid accumulation of metabolites. The pH (~9) and salinity (~16 psu) of the Os doped seawater culture medium did not appreciably change from that of the natural seawater collected from Staithes, which is also ~9, and remained constant throughout the culture experiments. The recorded pH is higher than the normal pH range of seawater. This is probably due to the higher levels of photosynthesis relative to respiration during the day or, dissolution of carbonates from the surrounding bedrock. Following the culture experiment, each sample was oven-dried at 60 °C for 24 h and ground into a powder with an agate mortar and pestle.

2.3 Re-Os analysis

2.3.1 Macroalgae

The Re-Os abundance and isotope composition determinations for all *F. vesiculosus* samples were obtained by isotope-dilution negative ion mass spectrometry (ID-NTIMS) at the Durham Geochemistry Centre in the Laboratory for Sulphide and Source Rock Geochronology and Geochemistry. Approximately 80 to 100 mg of sample powder was utilised for the Re-Os analysis. The powdered sample was added to a Carius tube with a known amount of a mixed ^{185}Re + ^{190}Os tracer solution. To prevent any sample reaction prior to sealing, the Carius tubes were placed into an ethanol/dry ice bath and 3 mL of 11 N HCl and 6 mL of 15.5 N HNO_3 were added. After sealing, the Carius tubes were placed into an oven and heated to 220 ºC for 24 h. The Os was isolated from the acid medium using $CHCl_3$ solvent extraction, with the Os back extracted into HBr. The Os was further purified using a CrO_3-H_2SO_4 – HBr micro-distillation methodology (Birck et al., 1997; Cohen and Waters, 1996). The resultant Re-bearing acid medium was evaporated to dryness at 80 ˚C, with the Re isolated and purified using both NaOH-acetone solvent extraction and HNO_3-HCl anion chromatography (Cumming et al., 2013).

2.3.2 Seawater

The Os abundance and isotope composition of the seawater at Staithes was determined using the liquid bromine (Br_2) methodology (Gannoun and Burton, 2014) at the Laboratoire Magmas et Volcans at the Campus Universitaire des Cézeaux. In brief, ~60 g of water sample, plus a known amount of mixed (^{190}Os + ^{185}Re) tracer solution, together with 2 mL of Br_2, 2 mL of CrO_3-H_2SO_4 solution and 1.5 mL of 98% H_2SO_4 were sealed into a 120 mL Savillex vial and heated to 100˚C in an oven for 72 h. Following the spike-sample equilibrium stage, to test that excess Cr^{6+} still exists in the CrO_3-H_2SO_4 solution, a drop (~30 µl) of the aqueous phase was pipetted and added to

3% v/v H_2O_2 solution. This resulted in the CrO_3 reacting with the H_2O_2 by producing intense bubbling with a transient dense blue colour formed, thus confirming the presence of excess Cr^{6+}. Osmium was extracted from the sample into liquid Br_2. To increase the extraction yield of Os, a second extraction of Os was conducted using 1 ml of Br_2. The 1 mL of liquid Br_2 was added to the sample solution reacted for 1 hr and then removed. The extracted Br_2 was mixed with 1 ml of 9N HBr and evaporated to dryness. The Os was further purified using a CrO_3-H_2SO_4 – HBr micro-distillation. The Os extracted, Re-bearing solution was evaporated to dryness. The Re was purified as described for the macroalgae samples (NaOH-acetone solvent extraction and HNO_3-HCl anion chromatography, Cumming et al., 2013) at the laboratories at the Durham Geochemistry Centre.

2.4 Mass spectrometry

The purified Re and Os fractions were loaded onto Ni and Pt filaments, respectively and measured using NTIMS (Creaser et al., 1991; Völkening et al., 1991) on a Thermo Scientific TRITON mass spectrometer using Faraday collectors in static mode, and an electron multipler in dynamic mode, respectively. The Re and Os abundances and isotope compositions are presented with 2 sigma absolute uncertainties which include full error propagation of uncertainties in the mass spectrometer measurements, blank, spike and sample and spike weights. Full analytical blank values for the macroalgae analysis are 2.4 ± 0.04 pg for Re, 0.05 ± 0.02 pg for Os, with a $^{187}Os/^{188}Os$ composition of 0.25 ± 0.15 (1 SD, n = 3). For the seawater analysis the full analytical blank values are 10.0 ± 1.3 pg for Re, 0.043 ± 0.002 pg for Os, with a $^{187}Os/^{188}Os$ composition of 0.72 ± 0.02 (1 SD, n = 4).

To monitor the long-term reproducibility of mass spectrometer measurements Re and Os (DROsS, DTM) reference solutions were analysed. The 125 pg Re solution yields an average ^{185}Re/^{187}Re ratio of 0.5983 ± 0.0024 (2 SD., n = 5), which is in agreement with the published values (e.g., Cumming et al., 2013). A 50 pg DROsS solution gave an ^{187}Os/^{188}Os ratio of 0.16088 ± 0.0008 (2 SD., n = 5), which is in agreement with the reported value for the DROsS reference solution (Nowel et al., 2008). For the seawater Os analysis at the Laboratoire Magmas et Volcans instrument reproducibility is monitored using a 1 pg DTM Os solution, which yields an ^{187}Os/^{188}Os value of 0.1740 ± 0.0002 (2 SD, n = 4), which is inagreement with published values (Chen and Sharma, 2008; Gannoun and Burton, 2014).

3. Results

3.1 Re and Os abundances and isotope compositions of Staithes seawater

The Staithes seawater possesses a Re and Os abundance of 8.2 and 0.0156 ppt, respectively, with a ^{187}Re/^{188}Os value of 2790.6 ± 49.7 and a ^{187}Os/^{188}Os composition of 0.94 ± 0.04 (Table 1). The filtered seawater was doped with DROsS to create a seawater culture solution with an Os concentration 3× (~0.05 ppt), 6× (~0.1 ppt) and 200× (~3 ppt) that of seawater, which respectively have ^{187}Os/^{188}Os compositions of 0.38 ± 0.02, 0.29 ± 0.01, and 0.18 ± 0.01 (Table 2).

3.2 Re and Os abundances and isotope compositions within *F. vesiculosus* structures

The natural total Os abundance within all structures of *F. vesiculosus* collected during May 2014 directly from the seaward side of the Staithes harbour wall and not cultured, is between 1600 and 3700 times greater than the concentration found in seawater (Fig. 1). The Os abundance in the *F. vesiculosus* structures ranges from 16 to

38 ppt (Fig. 1; Table 1). The structure that contains the least amount of Os is the holdfast (16 ppt), with the blades possessing the highest Os abundance (38 ppt). The remaining structures (tips, stipe and vesicles) possess similar concentrations (24 and 25 ppt Os). A mixture of all the *F. vesiculosus* structures possesses ~34 ppt Os, which is reasonable if we take the value as a reference as the approximate relative proportions of each structure of *F. vesiculosus*. For example, *F. vesiculosus* is comprised of 67 % tips and blades, 30 % stipe and vesicles and 3 % holdfast (Fig. 1).

A previous study showed that the the natural Re abundance within *F. vesiculosus* varies (23 to 313 ppb) and that Re is not located in one specific structure (Racionero-Gómez et al. 2016). In agreement with this previous study, we show that the Re abundance is highly variable throughout *F. vesiculosus*, with Re abundances ranging from ~22 to 138 ppb, being between 3100 to 19700 times greater than that found in seawater (Table 1). Similar to Os, the holdfast (and stipe) possess the least amount of Re (~22 ppb). However, in contrast to Os, the tips possess the greatest enrichment of Re (~138 ppb).

The variability in Re and Os abundance means that the ^{187}Re/^{188}Os values for *F. vesiculosus* structures is highly variable (Table 1). The ^{187}Re/^{188}Os values range between ~4672 (stipe) and 30558 (tips), with the holdfast and blades possessing similar values to those of the stipe. The ^{187}Os/^{188}Os values for the *F. vesiculosus* structures, with the exception of the holdfast, possesses an average composition of 0.80 ± 0.03 (1 SD) that reflects a moderately radiogenic composition; this is identical, within uncertainty, to the mixture of all the structures (0.81 ± 0.04).

3.3 **Uptake of Osmium by *F. vesiculosus* culture tips**

The natural Os abundance of the tips of a specimen of *F. vesiculosus* collected in June 2015 possesses significantly less Os (7.8 ppt; Table 1) than that of the same structure from a specimen collected in May 2014 (23.5 ppt; Table 1). The same is observed for rhenium (138 ppb for May 2014 versus 47 ppb for June 2015; Table 1). This difference can be due to many different factors; location, yearly, monthly or daily changes, ocean sediment turbulence, age of the specimen and other present unknown conditions (Horta-Puga et al., 2013; Lyngby and Brix, 1982). Furthermore, to our knowledge the impacts that each specific factor produces to the flux of Re and Os to the nearshore have not been determined. Although the Re and Os abundances are different between the samples collected in May 2014 and June 2015, the ^{187}Re/^{188}Os compositions are similar (~30558 ± 2046 (May 2014) versus ~34794 ± 2074 (June 2015). The ^{187}Os/^{188}Os compositions are slightly different (0.75 ± 0.05 (May 2014) vs 0.91 ± 0.07 (June 2015); Table 2), which likley reflects their geographic positions. For example, the June 2015 samples are taken from within the Harbour at the mouth of Staithes Beck, whereas the May 2014 samples are seaward of the Harbour wall (see Section 4.2).

The tips of the *F. vesiculosus* collected in June 2015 were used for the culture experiments. For all the culture experiments the Re abundance of the tips (~67 to 79 ppb) is greater than that from specimen tips analysed directly from the ocean (~47 ppb) (Table 1). We note that the only Re present in the culture media is that present in the natural seawater (~8 pg/g; Table 1) because the Re abundance in the Os solution (DROsS) used to dope the natural seawater is negligible (e.g., 1 pg/g Os solution contains ~7e^{-6} fg/g Re (Nowell et al., 2008). The Re abundance of the cultured tips shows a decrease from ~79 ppb for the 3× experiment, to ~71 ppb for the 6× experiment, and ~67 ppb for the 200× experiment (Table 1).

For osmium, the abundance increases proportionally to the amount of Os doped in the seawater (3× = ~20 ppt, 6× = ~30 ppt, 200× = ~200 ppt; Table 1; Fig. 4). Coupled with this increase in Os abundance is a trend to less radiogenic ^{187}Os/^{188}Os compositions (3× = 0.35 ± 0.02, 6× = 0.28 ± 0.01, 200× = 0.18 ± 0.00; Table 1; Fig. 4). Additionally, as a direct result of the overall increase of Os in the cultured tips with a relatively similar Re abundance, the ^{187}Re/^{188}Os composition significantly decreases (natural sample = ~32000; 3× = ~18000, 6× = ~12000, 200× = ~1600; Table 1).

4. Discussion and implications

4.1 Localization and uptake of Os within *F. vesiculosus*

Five types of cells can be distinguished in brown macroalgae: epidermal cells, primary cortical cells, secondary cortical cells, medullary cells and hyphae (Davy de Virville and Feldmann, 1961). A previous study identified that Re accumulation in *F. vesiculosus* is variable across the structural components (holdfast, blade, stipe, tips) of the macroalgae, indicating that there were some cells/structures more specialized for the uptake of Re (Racionero-Gómez et al. 2016). In the case of Os, its abundance does not signifcantly vary between structures, with the exception of the holdfast, suggesting that there is no specific cell specialization for the uptake of Os (Fig. 1; Table 1). The holdfast does not serve as the primary organ for water or nutrient uptake, instead it serves to anchor the macroalgae to the substrate. Therefore, lower Os abundances in the holdfast are expected. Moreover, it is suggested that Re could be biologically influenced (Racionero-Gómez et al. 2016), with uptake controlled by the growing season, as observed for zinc, lead and copper (Riget et al., 1995, Fuge and James, 1973). As such, this may also be the case for Os, however we cannot conclusively state that Os uptake is biologically controlled, because our samples were collected principally during the same growing season. Although, this may explain, in part, the varaibility in Re and Os abundance between the May 2014 and June 2015 samples as noted above. Nevertheless, the uptake of Os by *F. vesiculosus* is similar to that of Re, in the sense that, it is currently known to have no biological role. Further, the difference in Os isotopic composition between each structure cannot be considered significant given that all values overlap within uncertainty, with the exception of the holdfast (see Table 1).

The measured Os abundance in the cultured *F. vesiculosus* tips show a positive correlation with the concentration of Os doped seawater (see Tables 1, 2; Fig. 4). The culture experiment with the highest Os concentration (200× (3 ppt Os) seawater), resulted in tips possessing an Os abundance of ~194 ppt, which is ~25 times higher than the background concentration of Os in the specimens collected (Table 1).

Using the ^{187}Os/^{188}Os composition of the Staithes seawater (0.94 ± 0.04), together with the background Os abundance in the tips of the June 2015 collection (~8 ppt; Table 1), with the concentration of the doped seawater and cultured tips and their ^{187}Os/^{188}Os composition, we observe that the percentage of Os that has been transferred from seawater to the algae is about 17 % (Table 2).

Coincident with the increase in Os abundance within the culture experiments is the decrease in Re (Table 1), indicating possible competition between similar cell binding sites or uptake pathways between Re and Os, both forming oxoanions in seawater. However, the uptake pathways and binding sites of Re have not yet been identified, thus it is currently not known where Os accumulates in *F. vesiculosus*.

4.2 Implications of the ^{187}Os/^{188}Os isotope composition of *F. vesiculosus*

The ^{187}Os/^{188}Os composition of *F. vesiculosus* in a natural setting from the harbour at Staithes is 0.91 ± 0.07 (Table 1; Fig. 4) based on results from specimens collected in June 2015, which is within uncertainty to that of the seawater from the same location (0.94 ± 0.04) (Table 1). The agreement of the *F. vesiculosus* and seawater $^{187}Os/^{188}Os$ compositions would imply that macroalgae records the $^{187}Os/^{188}Os$ composition of the watermass it is living in. This is further supported by the culture experiments. For each culture experiment the measured $^{187}Os/^{188}Os$ composition of the tips coincides with the $^{187}Os/^{188}Os$ composition of doped seawater (Table 2; Fig. 4). This indicates that the $^{187}Os/^{188}Os$ composition of seaweed reflects the media in which it grows, and thus directly supports the use of *F. vesiculosus* (and macroalgae) as a biological proxy for the $^{187}Os/^{188}Os$ composition in seawater (Rooney et al, 2016). For example, the $^{187}Os/^{188}Os$ composition for three floating macroalgae (*Sargassum fluitans* and *S. natans*) collected from three different locations ~300 miles offshore in the Gulf of Mexico (1.05 ± 0.01; Rooney et al, 2016) are coincident with that of the present day open oceanic $^{187}Os/^{188}Os$ value of 1.06 (1.04 for the North Atlantic and Central Pacific; 1.06 for the Eastern Pacific and Indian Ocean) determined from direct analyses of seawater and of hydrogenetic Fe-Mn crusts (see Peucker-Ehrenbrink and Ravizza, 2000 and references therein; Gannoun and Burton, 2014 and references therein). In contrast, macroalgae from the coast of the Disko Bugt and Uummannaq regions of the west coast of Greenland show deviations from the $^{187}Os/^{188}Os$ composition of the open ocean (between 0.9 and 1.9) which directly relate to Os flux (abundance and isotope compositon) into the coastal region (Rooney et al., 2016). The latter together with the slightly lower and variable $^{187}Os/^{188}Os$ composition (~0.91 (June 2015 Staithes harbour) vs ~0.81 (Staithes east of the harbour wall); Table 1) of the macroalgae from Staithes in comparison to that of the open sea may suggest that the Os isotope composition of macroalgae is strongly controlled by its proximity to the coast, riverine input and regional variations in the Os flux (i.e., abundance and isotope composition) into the ocean, as also shown along the transects of estuaries (e.g., Levasseur et al., 2000; Martin et al., 2001; Sharma et al., 2007). For example, the Fly River Estuary reflects the input of unradiogenic Os and shows an increasing ^{187}Os/^{188}Os composition oceanward from 0.61 to 0.91 (Martin et al., 2001). In contrast, the Lena River Estuary and the Godavari Delta reflects the input of radiogenic Os, with the ^{187}Os/^{188}Os value decreasing oceanward from 1.55 to 1.13, and 1.30 to 0.90, respectively (Levasseur et al., 2000; Sharma et al., 2007). Moreover, surface seawater has a distinctly lower ^{187}Os/^{188}Os than the deep ocean (Chen et al., 2009; Gannoun and Burton, 2014). Therefore, macroalgae from distinct oceanic settings (e.g., coastal, estuarine versus open ocean) provides the ability to record the ^{187}Os/^{188}Os composition of seawater in addition to direct seawater and sediment analysis to further access the factors (e.g., geological and anthroprogenic) controlling the ^{187}Os/^{188}Os composition of seawater.

4.3 Implications of the ^{187}Re/^{188}Os isotope composition of *F. vesiculosus*

In addition to the ^{187}Os/^{188}Os composition of macroalage, the ^{187}Re/^{188}Os values of macroalgae (this study; Rooney et al., 2016) may provide insight into the variability of the ^{187}Re/^{188}Os in sediments as organic matter. The ^{187}Re/^{188}Os values for staithes seawater (2790.6 ± 49.7) falls somewhere between open ocean (4270; Anbar et al., 1992; Coloder et al., 1993; Sharma et al., 1997; Levassuer et al., 1998; Woodhouse et al., 1999; Peucker-Ehrenbrik and Ravizza, 2000) and riverine (227; Coloder et al., 1993b; Sharma and Wasserburg, 1997; Levassuer et al., 1999; Peucker-Ehrenbrik and Ravizza, 2000) estimates, as expected for estuarine conditions. However, the ^{187}Re/^{188}Os values of macroalgae from this study (34794.1 ± 2074.4) are far higher suggesting that the ^{187}Re/^{188}Os ratios in macoralgae are not proportional to the seawater in which they live, but controlled by the uptake mechanism(s) of macroalgae that are currently unknown.

To date, it is known that the Re abundance in macroalgae can be highly variable (sub ppb to tens of ppb; Scadden, 1969; Yang, 1991; Mas et al., 2005; Prouty et al., 2014; Racionero-Gómez et al., 2016; Rooney et al., 2016). For osmium, the results thus far also indicate that the Os abundance in macroalgae can also be highly variable (this study; Rooney et al, 2016). Further, in addition to macroalgae that are components of sediment organic matter, microorganisms can also accummulate Re (Prouty et al., 2014; Mashkani et al., 2009; Ghazvini and Mashkani, 2009), although to date, no data exists for osmium. Given the variability of Re and Os uptake by macroalgae, the ^{187}Re/^{188}Os composition of macroalgae is seen to range from ~10 to ~35,000 (this study; Rooney et al., 2016). Metabolically inactive (i.e dead) macroalgae (*F. vesiculosus*) does not appreciably accummulate rhenium (Racionero-Gómez et al., 2016). If Os in metabolically inactive macroalgae and/or microogranisms is not accumulated or released, then the Re and Os abundance, and isotope composition could be dominantly controlled by the abundance, variability, and the structural type of the organisms preserved in a sediment as organic matter rather than purely sequestration at the sediment-water interface (Yamashita et al., 2007 and references therein). As such, organic matter and organic type, in addition to the depositional setting conditions (Yamashita et al., 2007; Georgiev et al., 2011), maybe important factors in controlling Re/Os fractionation observed in organic-rich sediments (Cumming et al., 2012; Harris et al., 2012).

A further implication of the uptake of Re and Os by organisms could be its effect on the Re-Os organic-rich sedimentary geochronology. In addition to the Re-Os isotope system remaining undisturbed and for the samples to possess a range in

^{187}Re/^{188}Os values, the stratigraphic interval must possess similar initial ^{187}Os/^{188}Os values to provide reliable (accurate and precise) dates of sediment deposition (Cohen et al., 1999; Selby and Creaser, 2003). As such the heterogenous mixing of organisms with variable ^{187}Os/^{188}Os compositions in a sedimentary rock could hamper the ability to yield precise Re-Os dates. This could be particularly problematic in nearshore depositional settings of organic-rich sediments. For example, in a estuarine or deltaic sedimentary system the ^{187}Os/^{188}Os composition is variable along its transect (Levasseur et al., 2000; Martin et al., 2001; Sharma et al., 2007). Further, macroalgae from Greenland within Disko Bay show a 0.05 difference in their ^{187}Os/^{188}Os composition (Rooney et al., 2016). As such, organisms along the transect may also have variable ^{187}Os/^{188}Os compositions. Therefore any heterogeneous mixing of organisms that are preseved as organic matter within a sediment with different ^{187}Os/^{188}Os compositions could impact on the precision of Re-Os organic-rich sedimentary geochronology.

5. Conclusions

Culture experiments indicate that macroalgae acquires the ^{187}Os/^{188}Os composition of the media in which it grows. As a result this suggests that macroalgae are a viable biological proxy to determine the ^{187}Os/^{188}Os composition of seawater in various oceanographic settings. Specifically in coastal settings the ^{187}Os/^{188}Os composition of macroalgae could be used to assess the ^{187}Os/^{188}Os composition of continental input in to the ocean.

Acknowledgements

We wish to express special thanks to Dr Joanna Hesselink for technical support and to John Bothwell and the Faculty of Biological Sciences of Durham for the laboratory support. We are very grateful to OEA Labs Ltd for funding the project. Nancy Prouty is thanked for her constructive comments, as are the remarks of two GCA reviewers, which helped improve this manuscript.

References

Anbar A.D. Creaser R.A. Papanastassiou D.A. and Wasserburg G.J. (1992) Rhenium in seawater: confirmation of generally conservative behavior. *Geochim. Cosmochim. Acta* **56**, 4099-4103.

Banner J.L. (2004) Radiogenic isotopes: systematics and applications to earth surface processes and chemical stratigraphy. *Earth-Science Reviews* **65**, 141-194. DOI 10.1016/S0012-8252(03)00086-2

Birck J.L. Roy-Barman M. and Capmas F. (1997) Re–Os isotopic measurements at the femtomole level in natural samples. *Geostand Newstett* **20**, 19-27. DOI 10.1111/j.1751-908X.1997.tb00528.x

Bryan G.W. (1983) Brown seaweed, *Fucus vesiculosus*, and the gastropod, *Littorina littoralis*, as indicators of trace-metal availability in estuaries. *Sci. Total Environ.* **28**, 91-104. DOI 10.1016/S0048-9697(83)80010-2

Carlson L. (1991) Seasonal variation in growth, reproduction and nitrogen content of *Fucus vesiculosus* in the Öresund, Southern Sweden. *Bot. Mar.* **34**, 447-453. DOI 10.1515/botm.1991.34.5.447

Chapman V. and Chapman D. (1980) Seaweeds and their uses, 3rd ed, New York.

Chen C. and Sharma M. (2009) High precision and high sensitivity measurements of osmium in seawater. *Anal. Chem.* **81**, 5400-5406. DOI 10.1021/ac900600e

Cohen A.S. Coe A.L. Barlett J.M. and Hawkesworth C.J. (1999) Precise Re-Os ages of organic-rich mudrocks and the Os isotope composition of Jurassic seawater. *Earth Planet Sc. Lett.* **167**, 159–173. DOI 10.1016/S0012-821X(99)00026-6

Cohen A.S. Coe A.L. Harding S.M. and Schwark L. (2003) Osmium isotope evidence for the regulation of atmospheric CO_2 by continental weathering. *Geol. Soc. Am.* **32**, 157-160. DOI 10.1130/G20158.1

Cohen A.S. and Waters F.C. (1996) Separation of osmium from geological materials by solvent extraction for analysis by thermal ionisation mass specrrometry. *Anal. Chim. Acta* **332**, 269-275. DOI 10.1016/0003-2670(96)00226-7

Colodner D.C. Boyle E.A. and Edmond J.M. (1993a) Determination of rhenium and platinum in natural waters and sediments, and iridium in sediments by flow injection isotope dilution inductively coupled plasma mass spectrometry. *Analyt.Chem*. **65**, 1419-1425.

Colodner D. Sachs J. Ravizza G. Turekian K.K. Edmond J. and Boyle E. (1993b) The geochemical cycle of rhenium: a reconnaissance. *Earth Planet. Sci.Lett.* **117**, 205-221.

Cotton F.G. and Wilkinson G. (1998) Advanced Inorganic chemistry, 5th edition, J. Wiley & Sons.

Creaser R.A. Papanastassiou D.A. and Wasserburg G.J. (1991) Negative thermal ion mass spectrometry of osmium, rhenium and iridium. *Geochim. Cosmochim. Acta* **55**, 397-401. DOI 10.1016/0016-7037(91)90427-7

Cumming V. M. Selby D. and Lillis P.G. (2012) Re-Os geochronology of lacustrine organic-rich sedimentary rocks: insights into direct depositional dating of lacustrine successions. Re-Os systematics and paleocontinental weathering. *Earth Planet. Sc. Lett.* **359–360**, 194–205. DOI 10.1016/j.epsl.2012.10.012

Cumming V.M. Poulton S.W. Rooney A.D. Selby D. (2013) Anoxia in the terrestrial environment during the Late Mesoproterozoic. *Geology*. DOI 10.1130/G34299.1

Davis T.A. Volesky B. and Mucci A. (2003) A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res.* **37**, 4311-4330. DOI 10.1016/S0043-1354(03)00293-8

Davy de Virville A. and Feldmann J. (1961) IV International Symposium on Seaweed. Pergamon press, Biarritz.

Fuge R. and James K.H. (1973) Trace metal concentrations in brown seaweeds, Cardigan Bay, Wales. *Mar. Chem.* **1**, 281-293. DOI 10.1016/0304-4203(73)90018-2

Gannoun A. and Burton K.W. (2014) High precision osmium elemental and isotope measurements of North Atlantic seawater. *J. Anal. Atom. Spectrom.* **29**, 2330-2342. DOI 10.1039/c4ja00265b

Georgiev S. Stein H.J. Hannah J.L. Bingen B. Weiss H.M. and Piasecki S. (2011) Hot acidic Late Permian seas stifle in record time: *Earth Planet. Sc. Lett.* **310**, 389-400. DOI 10.1016/j.epsl.2011.08.010

Graham L.E. and Wilcox L.W. (2000) Algae. United States of America.

Ghazvini P.T.M. and Mashkani S.G. (2009) Screening of bacterial cells for biosorption of oxyanions: Application of micro-PIXE for measurement of biosorption. *Hydrometallurgy* **96**, 246-252. DOI 10.1016/j.hydromet.2008.10.012

Gustow L. Rahman M.M. Bartl K. Saborowski R. Bartsch I. and Wiencke C. (2014) Ocean acidification affects growth but not nutritional quality of the seaweed *Fucus vesiculosus* (Phaeophyceae, Fucales). *J. Exp. Mar. Biol. Ecol* **453**, 84-90. DOI 10.1016/j.jembe.2014.01.005

Harris N.B. Mnich C.A. Selby D. and Korn D. (2012) Minor and trace element and Re-Os chemistry of the upper Devonian woodford shale, permian basin, West Texas: insights into metal abundance and basin processes. *Chem. Geol.* **356**, 76–93. DOI 10.1016/j.chemgeo.2013.07.018

Hiscock S. (1991) Brown seaweeds. A field key to the british., Shrewsbury, Montford Bridge.

Horta-Puga G. Cházaro-Olvera S. Winfield I. Avila-Romero M. and Moreno-Ramírez M. (2013) Cadmium, copper and lead in macroalgae from Veracruz Reef System, Gulf of Mexico: Spatial distribution and rainy season variability. *Mar. Pollut. Bull.* **68**, 127-133. DOI 10.1016/j.marpolbul.2012.12.008

Karez C.S. Magalhaes V.F. Pfeiffer W.C. and Amado Filho G.M. (1994) Trace metal accumulation by algae in Sepetiba Bay, Brasil. *Environ. Pollut.* **83**, 351-356. DOI 10.1016/0269-7491(94)90157-0

Koide M. Goldberg E.D. and Walker R. (1996) The analysis of seawater osmium. *Deep Sea Reasources* **43**, 53-55. DOI 10.1016/0967-0645(95)00082-8

Levasseur S. Birck J.-L. and Allègre C.J. (1998) Direct measurement of femtomoles of osmium and the ^{187}Os/^{186}Os ratio in seawater. *Science* **282**, 272-274. DOI 10.1126/science.282.5387.272

Levassuer S. Birck J.-L. and Allègre C.J. (1999) The osmium riverine flux and the oceanic mass balance of osmium. *Ear. Planet.Sci.Lett.* **174**, 7-23.

Levasseur S. Rachold V. Birck J.L.and Allègre C.J. (2000) Osmium behavior in estuaries: The Lena River Example. *Earth Planet. Sci. Lett.* **177**(3– 4), 227– 235. DOI 10.1016/S0012-821X(00)00049-2

Lobban C.S. and Harrison P.J. (1994) Seaweed Ecology and Physiology. Press syndicate of the university of Cambridge, Cambridge University.

Lyngby J.E. and Brix H. (1982) Seasonal and environmental variation in cadmium, copper, lead and zinc concentrations in eelgrass (*Zostera marina L.*) in the Limfjor,k Denmark. *Aquat. Bot.* **14**, 59-74. DOI 10.1016/0304-3770(82)90086-9

Martin C.E. Peucker-Ehrenbrink B. Brunskill G. Szymczak R. (2001) Osmium isotope geochemistry of a tropical estuary. *Geochim. Cosmochim. Acta* **65**(19), 3193–3200.

Mas J.L. Tagami K. Uchida S. (2005) Rhenium measurements on North Atlantic seaweed samples by ID-ICP-MS: An observation on the Re concentration factors. *J. Radioanal. Nucl. Ch.* **265**: 361–365. DOI 10.1007/s10967-005-0833-3

Mashkani S.G. Ghazvini P.T.M. Aligol D.A. 2009. Uptake of Re(VII) from aqueous solutions by *Bacillus* sp. GT-83-23. *Bioresource Technol.* **100**, 603-608. DOI 10.1016/j.biortech.2008.06.065

Morries A.W. and Bale A.J. (1975) The accumulation of cadmium, copper, manganese and zinc by *Fucus vesiculosus* in the Bristol Channel. *Estuar. Coast. Mar. Sci.* **3**, 153-163. DOI 10.1016/0302-3524(75)90018-3

Nowell G.M. Luguet A. Pearson D.G. and Horstwood M.A. (2008) Precise and accurate ^{186}Os/^{188}Os and ^{187}Os/^{188}Os measurements by multi-collector plasma ionisation mass spectrometry (MC-ICP-MS) part I: solution analyses. *Chem. Geol.* **248**, 363-393. DOI 10.1016/j.chemgeo.2007.10.020

Palmer M.R. Falkner K.K. Turekian K.K. and Calvert S.E. (1988) Sources of osmium isotopes in manganese nodules. *Geochim. Cosmochim. Acta* **52**, 1197-1202. DOI 10.1016/0016-7037(88)90274-8

Peucker-Ehrenbrink B. and Ravizza G. (2000) The marine osmium isotope record. *Terra Nova* **12**, 205-219. DOI 10.1046/j.1365-3121.2000.00295.x

Peucker-Ehrenbrink B. and Jahn B.-m. (2001) Rhenium-osmium isotope systematics and platinum group element concentrations: Loess and the upper continental crust. *Geochem. Geophy. Geosy*. **2** Paper number 2001GC000172

Prouty N.G. Roark E.B. Koenig A. Demopoulos A.W. Batista F.C. Kocar B.D. Selby D. McCarthy M.D. and Mienis F. (2014) Deep-sea coral record of human impact on watershed quality in the Mississippi River Basin. *Global Biochem. Cy.* **28** DOI 10.1002/ 2013GB004754.

Racionero-Gómez B. Sproson A.D. Selby D. Gröcke D.R. Redden H. and Greenwell H.C. (2016) Rhenium uptake and distribution in Phaeophyceae macroalgae, *Fucus vesiculosus*. Royal journal of interface. *Royal Society Open Science*, in press

Ragan M.A. Smidsrod O. and Larsen B. (1979) Chelation of divalent metal ions by brown algal polyphenols. *Mar. Chem.* **7**, 265-271. DOI 10.1016/0304-4203(79)90043-4

Rainbow P.S. and Phillips D.J.H. (1993) Cosmopolitan biomonitors of trace metals. *Mar. Pollut. Bull.* **26**, 593-601. DOI 10.1016/0025-326X(93)90497-8

Raize O. Argaman Y. and Yannai S. (2004) Mechanisms of biosorption of different heavy metals by brown marine macroalgae. *Biotechnol. Bioeng.* **87**, 451-458. DOI 10.1002/bit.20136

Rawson P.F. and Wright J.K. (2000) The Yorkshire Coast. Geologists' Association Guide No. 34. The Geologists' Association, Burlington House, Piccadilly, London. 130pp. With contributions by Starmer I.C. Whitham F. and Hemingway J.E. The Third Revised Edition, edited by Greensmith J.T.

Riget F. Johansen P. Asmund G. (1995) Natural seasonal variation of vadmium, copper, lead and zinc in brown seaweed (*Fucus vesiculosus*). *Mar. Pollut. Bull.* **30**, 409–413. DOI 10.1016/0025-326X(95)99847-W

Rooney A.D. Selby D. Lloyd J.M. Roberts D.H. Lückge A. Sageman B.B. and Prouty N.G. (2016) Using Osmium isotopes to track millennial-scale Holocene glacial advance and retreat: Insights from the Greenland Ice Sheet. *Quaternary Sci. Rev.* **138,** 49-61. DOI 10.1016/j.quascirev.2016.02.021

Scadden E. M. (1969) Rhenium: its concentration in Pacific Ocean surface waters. *Geochim. Cosmochim. Acta* **33**, 5: 633-637. DOI 10.1016/0016-7037(69)90019-2

Selby D. and Creaser R.A. (2003) Re-Os geochronology of organic rich sediments: An evaluation of organic matter analysis methods. *Chem. Geol.* **200**, 225-240. DOI 10.1016/S0009-2541(03)00199-2

Sharma M. Papanastassiou D.A. and Wasserbug G.J. (1997) The concentration and isotopic composition of osmium in the oceans. *Geochim. Cosmochim. Acta* **61**, 3287-3299. DOI 10.1016/S0016-7037(97)00210-X

Sharma M. and Wasserburg G.J. (1997) Osmium in the rivers. *Geochim. Cosmochim. Acta* **6**, 5411-5416.

Sharma M. Balakrishna K. Hofmann A.W. and Shankar R. (2007) The transport of osmium and strontium isotopes through a tropical estuary. *Geochim. Cosmochim. Acta* **71**, 4856-4867. DOI 10.1016/j.gca.2007.08.004

Sharma M. Chen C. and Blazina T. (2012) Osmium contamination of seawater samples stored in polyethylene bottles. *Limnol. Oceanogr.: Methods* **10**, 618-630. DOI 10.4319/lom.2012.10.618

Strömgren T. (1977) Short-term effect of temperature upon the growth of intertidal Fucales. *J. Exp. Mar. Biol. Ecol.* **29**. DOI 10.1016/0022-0981(77)90047-8

Völkening J. Walczyk T. and Heumann K.G. (1991) Osmium isotope ratio determinations by negative thermal ion mass spectrometry. *Int. J. Mass Spectrom.* **105**, 147-159.

Wedepohl K.H. (1995) The composition of the continental crust. *Geochim. Cosmochim. Acta* **59**, 1217-1232. DOI 10.1016/0016-7037(95)00038-2

White N. (2008) *Fucus vesiculosus*. Bladder wrack., in: [on-line]., M.L.I.N.B.a.S.K.I.S.-p. (Ed.), Plymouth: Marine Biological Association of the United Kingdom.

Woodhouse O.B. Ravizza G. Kenison Falker K. Statham P.J. and Peucker-Ehrenbrik B. (1999) Osmium in seawater: vertical profiles of concentration and isotopic composition in the eastern Pacific Ocean. *Earth Planet. Sc. Lett.* **173**, 223-233.

Yang J.S. (1991) High rhenium enrichment in brown algae: a biological sink of rhenium in the sea? *Hydrobiologia* **211**, 165–170. DOI 10.1007/BF00008532

Yamashita Y. Takahashi Y. Haba H. Enomoto S. Shimizu H. (2007) Comparison of reductive accumulation of Re and Os in seawater–sediment systems. *Geochim. Cosmochim. Acta* **71**, 3458–3475. DOI 10.1016/j.gca.2007.05.003

Figures and captions

Figure 1. Photo exhibiting the key structures of *F. vesiculosus*. Also shown are the Re and Os abundances, and Re-Os isotope compositions (Data including uncertainties are given in Table 1).

Figure 2. *F. vesiculosus* sample locations for May 2014 and June 2015.

Figure 3. Representation of culture growth set-up of non-reproductive *F. vesiculosus* thallus tips. (**A**) Two meshes were put inside each jar generating three levels that each hold three non-fertile tips each. (**B**) Photo of the culture jar used.

Figure 4. Osmium (ppt) accumulation (circles) and ^{187}Os/^{188}Os compositions (squares) in *F. vesiculosus* under different Os seawater culture media concentrations. The open symbols are for *F. vesiculosus* collected June 2015. See Tables 1 and 2 for data.

Table

Table 1. Rhenium (ppb), Osmium (ppt) and Re-Os isotope compositions in *F. vesiculosus* *s*tructures and culture experiment.

Sample	Weight (g)	Re (ppb)	Os (ppt)	^{187}Re/^{188}Os	^{187}Os/^{188}Os
May 2014 collection					
Tips	0,201	138.0 ± 0.7	23.5 ± 0.7	30558.8 ± 2046.6	0.75 ± 0.05
Blades	0,200	56.8 ± 0.3	37.6 ± 0.7	7902.1 ± 336.9	0.78 ± 0.04
Stipe	0,200	22.5 ± 0.2	25.2 ± 0.7	4672.6 ± 299.8	0.81 ± 0.05
Holdfast	0,200	21.6 ± 0.2	16.0 ± 0.7	7223.4 ± 736.2	0.95 ± 0.10
Vesicles	0,200	59.0 ± 0.4	24.8 ± 0.7	12476.6 ± 805.9	0.80 ± 0.05
Mix of structures	0,204	64.0 ± 0.7	33.8 ± 0.7	9930.3 ± 469.9	0.81 ± 0.04
June 2015 collection					
Tips	0,101	47.4 ± 0.1	7.8 ± 0.4	34794.1 ± 2074.4	0.91 ± 0.07
Culture experiment					
1- 3x seawater[1]	0,102	79.3 ± 0.2	21.2 ± 0.4	18585.9 ± 866.6	0.35 ± 0.02
2- 3x seawater[1]	0,101	77.7 ± 0.2	20.5 ± 0.1	18819.6 ± 757.5	0.34 ± 0.01
1- 6x seawater[1]	0,102	71.3 ± 0.2	28.6 ± 0.5	12235.8 ± 421.2	0.28 ± 0.01
2- 6x seawater[1]	0,102	71.1 ± 0.2	32.7 ± 0.5	10696.6 ± 323.4	0.28 ± 0.01
1- 200x seawater[1]	0,081	67.1 ± 0.2	201.6 ± 0.8	1615.0 ± 12.7	0.18 ± 0.00
2- 200x seawater[1]	0,081	66.8 ± 0.2	194.3 ± 0.8	1668.6 ± 13.4	0.18 ± 0.00
Staithes seawater					
seawater[2]	64,5	8.20 ± 0.08	15.7 ± 0.2	2790.6 ± 49.7	0.94 ± 0.04

[1] Culture experiment uses tips from specimens collected in June 2015

[2] seawater Re concentrations in ppt; Os concentrations given in ppq

All uncertainties are quoted at the 2s level

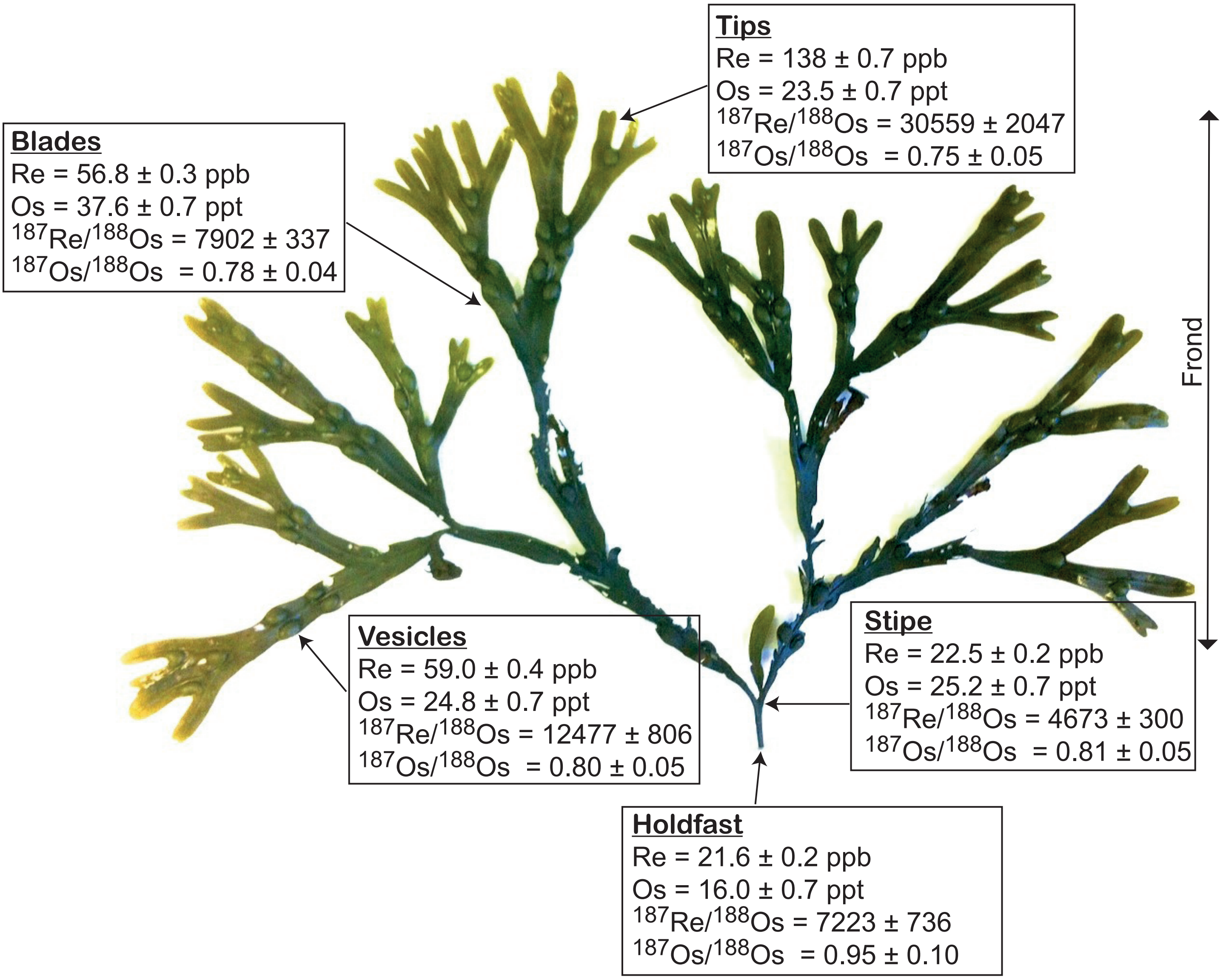
The Re-Os abundances are based on the dry mass of the seaweed

Table 2. Osmium (ppt) and 187Os/188Os compositions in the culture media and in *F. vesiculosus.*

Sample	**Seawater [Os] (ppt)**	**$^{187}Os/^{188}Os$ of seawater culture media**	**Measured $^{187}Os/^{188}Os$ of seaweed after culture growth**	**% of Os transferred from seawater culture media into the seaweed**
Natural seawater[1]	0,0156	0.94 ± 0.04		
3x seawater	0,05	0.38 ± 0.02	0.35 ± 0.02	17,4
6x seawater	0,1	0.29 ± 0.01	0.28 ± 0.01	16,8
200x seawater	3	0.18 ± 0.01	0.18 ± 0.00	16,9

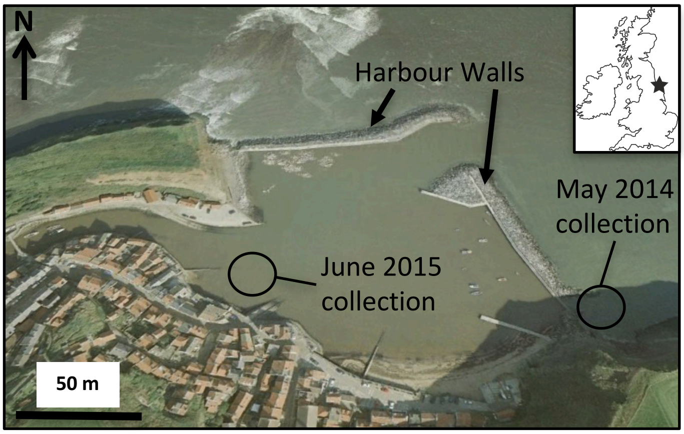
[1] Measured seawater from Staithes - see Table 1

Figure

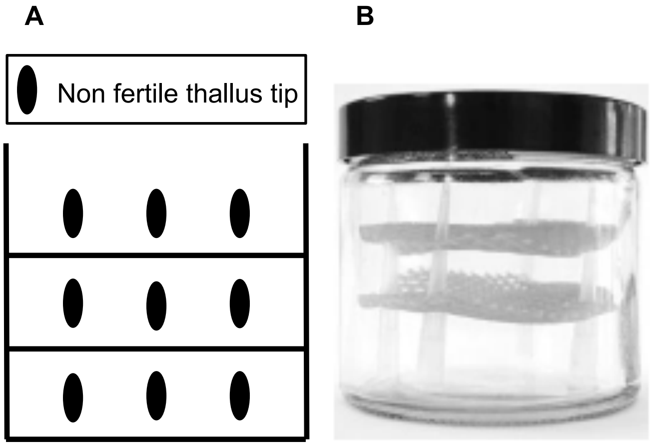


Tips
Re = 138 ± 0.7 ppb
Os = 23.5 ± 0.7 ppt
^{187}Re/^{188}Os = 30559 ± 2047
^{187}Os/^{188}Os = 0.75 ± 0.05
Blades
Re = 56.8 ± 0.3 ppb
Os = 37.6 ± 0.7 ppt
^{187}Re/^{188}Os = 7902 ± 337
^{187}Os/^{188}Os = 0.78 ± 0.04
Frond
Vesicles
Re = 59.0 ± 0.4 ppb
Os = 24.8 ± 0.7 ppt
^{187}Re/^{188}Os = 12477 ± 806
^{187}Os/^{188}Os = 0.80 ± 0.05
Stipe
Re = 22.5 ± 0.2 ppb
Os = 25.2 ± 0.7 ppt
^{187}Re/^{188}Os = 4673 ± 300
^{187}Os/^{188}Os = 0.81 ± 0.05
Holdfast
Re = 21.6 ± 0.2 ppb
Os = 16.0 ± 0.7 ppt
^{187}Re/^{188}Os = 7223 ± 736
^{187}Os/^{188}Os = 0.95 ± 0.10

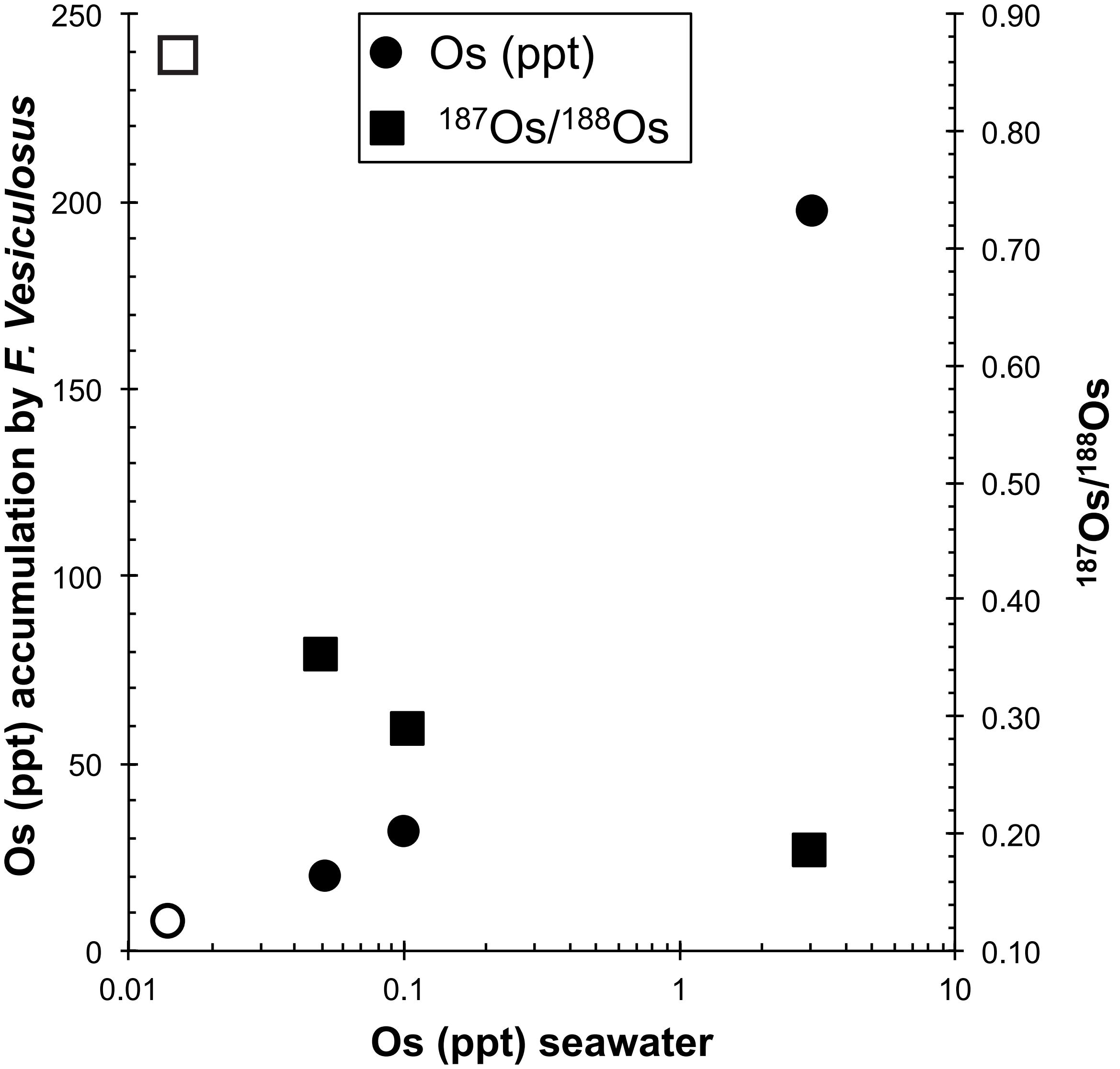
Figure


N
Harbour Walls
May 2014
collection
June 2015
collection
50 m

Figure



Figure


Os (ppt)
$^{187}Os/^{188}Os$
Os (ppt) accumulation by *F. Vesiculosus*
0
50
100
150
200
250
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
$^{187}Os/^{188}Os$
0.01
0.1
1
10
Os (ppt) seawater