

Macroalgae and sediments as records of seawater $^{187}\text{Os}/^{188}\text{Os}$ composition in the Long Island
Sound

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April 27, 2020

Abstract

Accurately measuring $^{187}\text{Os}/^{188}\text{Os}$ compositions of the sedimentary record and interpreting these geochemical proxies informs investigations of paleo-environments. Numerous studies rely on Re and Os as proxies for deep time intensity of continental weathering, global ocean oxygen levels, and periods of glaciation and deglaciation. Integral to these studies is an understanding of the Os residence time in seawater as well as how Re and Os behave in the modern and are incorporated into the sedimentary record in the modern through redox reactions and biological uptake. This paper presents new Re and Os isotope data from a core adjacent to the Connecticut coast in the Long Island Sound, as well as macro-algae (seaweed) sourced from the same site and distal Svalbard. Using isotope dilution negative thermal ionization mass spectrometry, we demonstrate that seaweed Re concentrations are orders of magnitude greater than that of sediments, suggesting that the biological uptake of Re and Os contributes significantly to our sedimentary archives. We show that both sediment records and seaweed are faithful geologic recorders of the oceanic Os composition. This adds to a body of evidence that supports the use of stratigraphic records to reconstruct past seawater conditions. Finally, our high-resolution data reveals variation in the Os composition of the Long Island Sound on timescales less than $\sim 10^3$ years, demonstrating that the residence time of Os in constrained basins is shorter than the canonical global ocean estimates of $\sim 10^4$ years. These results impact how we interpret the geologic record to reconstruct past environments and translate these interpretations to our projections for future climate change.

1. Introduction

A growing body of research is employing Osmium (Os) isotopes ($^{187}\text{Os}/^{188}\text{Os}$) to better understand paleoclimates, paleo-oceans, continental weathering patterns, and glacial-interglacial cycles (Peucker-Ehrenbrink and Ravizza 2000, Rooney et al. 2016, Stein and Hannah 2014). Os is one of the least abundant ocean elements, with an average concentration in the open ocean of only about .01 ppt (Gannoun and Burton). However, it is useful as a geochemical tracer of oceanic inputs from mantle, continental and potentially anthropogenic sources due to each source's unique Os isotopic signature. ^{187}Os decays radiogenically from ^{187}Re while ^{188}Os occurs without decay, but both isotopes behave chemically similarly (Stein and Hannah 2014).

Accurate measurement and interpretation of geochemical proxies like $^{187}\text{Os}/^{188}\text{Os}$ composition informs investigations of past climates, weathering, and glacial fluctuations. In turn, this understanding of paleoenvironments translates to better constrained estimates of glacial and oceanic climate change response.

Questions about the processes through which Os is incorporated in the sediment record limit our ability to interpret geochemical record (Racionero-Gomez 2016). Os is understood to be enriched in reducing sediments, but has also been shown to concentrate in the organic fraction (Peucker-Ehrenbrink and Ravizza 2012). Modern biological uptake of Re and Os can be used to better understand how the elements are eventually recorded in the sedimentary record. Recent studies have shown that macroalgae accurately records the Os isotope composition of its environment (Rooney 2016, Racionero-Gomez 2016). These studies suggest macroalgae is a useful biological proxy for the $^{187}\text{Os}/^{188}\text{Os}$ composition in various settings, but further analysis is

needed to observe this process in additional environments and determine the contribution of biological uptake to the sediment record of past ocean Os compositions.

Complete understanding of Os in the ocean is also limited in part by constraints on estimates for the residence time of Os in the oceans. Current estimates place the residence time at c. 10^4 years (Oxburgh 2001), but more recent studies have suggested that Os composition can change on shorter timescales of c. 10^3 years (Rooney 2016).

To better understand how the $^{187}\text{Os}/^{188}\text{Os}$ composition of seawater is recorded in the sediment record, we investigate the use of seaweed to constrain our estimate of the biological contribution of Os. This study focuses on two sets of biological samples: open-ocean brown macroalgae from the Long Island Sound FOAM study site, and coastal brown macroalgae from Svalbard. To investigate the Os residence time in the ocean, we also present sediment core data from the FOAM site.

2. Studied sites and sample material

Two study sites were used in this research. The proximal sediment and seaweed samples from the region of focus were collected at Yale's FOAM research center near Guilford, CT in the Long Island Sound. Distal seaweed samples were collected from off the coast of the Norwegian archipelago of Svalbard.

400 Nqpi "Krcpf"Uqwpf

Long Island Sound is an estuary mixture of freshwater, from primarily seven Connecticut rivers, and salt water from the Atlantic Ocean. It is ~160km long and ~30km wide with average depth 21m (Gay et al. 2004). The FOAM site at the location mapped in Figure 1 has been extensively studied by geologists at Yale for decades, and was chosen for its



Figure 1. Map of Long Island Sound showing location of FOAM site.

proximity, sediments known for enrichment in heavy metals, and historic discussion in the literature (Krishnaswami et al. 1984, Esser and Turekian 1993). The water column at the sampling site is ~9m deep and oxygenated (Esser and Turekian 1993).

400' HQCO 'ugf ko gpv'eqt g"

A 26cm core was taken from the surface sediments at the FOAM site during an September 2019 field work at the FOAM site. Sediments comprise shelly, brown to grey organic matter-bearing mud. Above depths of 10-12cm, sediments are bioturbated and oxic, while anoxic below (Esser and Turekian 1993). The FOAM sediments retain horizontal sedimentary features like laminae and shell layers, indicating there is minimal bioturbation below the surface layer and the sedimentary record is well-preserved chronologically (Krishnaswami et al. 1984). Based on radiocarbon dating of shell layers, net sediment accumulation rate for the top 0-15cm sediment at the FOAM site averaged $.03 \pm .021$ cm/year

(Krishnaswami et al. 1984). Using this sedimentation rate alone, our 26cm core would span about ~870yr BP. However, there are significant uncertainties associated with the use of this sedimentation rate to calculate sediment age. These uncertainties arise from surface particle mixing, the presence of shells containing bomb-related ^{14}C , and changing accumulation rates over time, with an average accumulation rate of $.094 \pm .021$ cm/year measured for depths 18-100cm (Krishnaswami et al. 1984). Cores taken during the 1984 study dated sediments at depths as shallow as 18cm at ~830yr BP. For the purposes of this study, where exact ages are unnecessary, it is reasonable to assume that our 26cm core spans less than approximately 1000yr BP.

4004'HQCO 'o cetq/cni cg"

Two brown macro-algae specimens from the *Cueqrj {mwo 'pqf quwo 'species were collected from the FOAM site in July and September 2019. This is a common species to rocky, sheltered shores and has a lifespan of up to ~15 years (White 2008). Specimens used in this study were fronds ~10-20cm long. The components of interest are the tips, blades, vesicles, and holdfast, outlined in Figure 2. "*

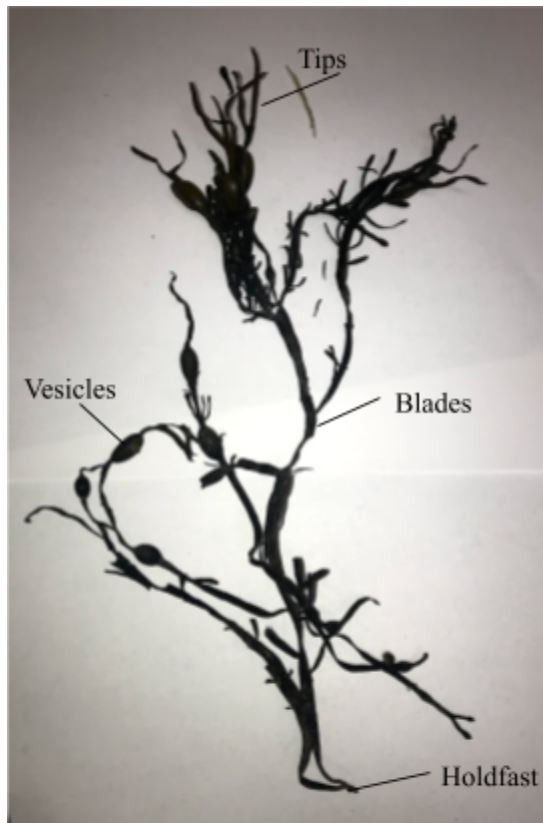


Figure 2. Photo of Long Island Sound specimen showing key structures of brown macroalgae.

4040 Uxndctf'''

Svalbard is an Arctic archipelago located north of Norway. This study uses samples from one of the major islands, Nordhaustlandet. The region is mountainous with numerous ice caps and glacial deposits (Ingolfsson).

4040Uxndctf "o cetq/cni cg"

Three brown macro-algae samples from the *Hwewu'Xgukewiqumu'* species were collected off the coast of Svalbard within the Brenevinsfjorden fjord during an August 2019 research expedition. This is also a common species found in the

North Sea, Baltic Sea, Atlantic and Pacific Oceans floating in the water column (Racionero-Gomez et al. 2016). It has similar components to that of the *Cueqrij (mw 'pqf quwo* 'shown in Figure 3, but without the characteristic two-pronged tips. It is less elastic and has smaller vesicles than the samples collected at the FOAM site. Its life span is much shorter, on the span of 3 to 5 years (Racionero-Gomez et al. 2016, White 2008).



Figure 3. Map of Svalbard study region, with locations of seaweed collection marked. (Norwegian Polar Institute)

The bedrock geology surrounding this region, shown in figure 4, is composed of sedimentary and intrusive rock dating to the Mesoproterozoic, as well as some igneous rock dating to the Ordovician to Devonian period. This is the rock that

glaciers are weathering and ultimately become inputs to the Brenevinsfjorden fjord studied.

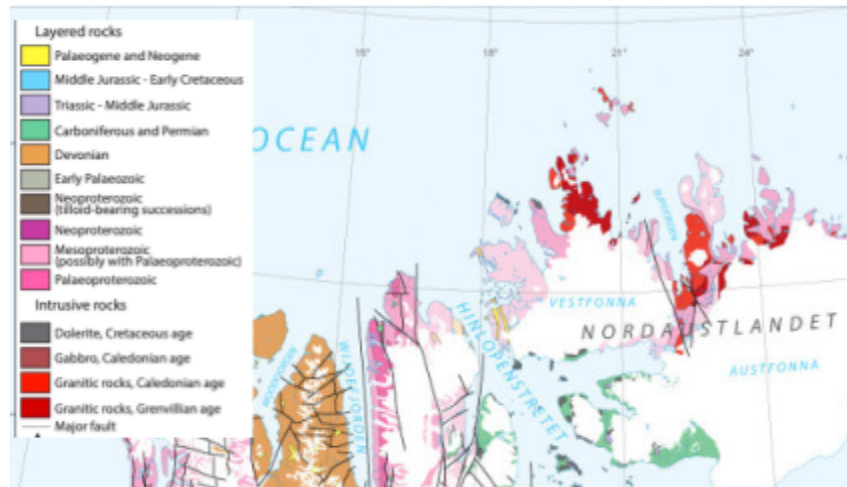


Figure 4. Map of bedrock geology in Svalbard, with study region marked. (Norwegian Polar Institute)

3. Methods

500 Uco rrg"rtgrctc v k p " c p f " r q y f g t k p i "

The FOAM core was separated into 26 1-cm samples utilizing an incremental core extruding apparatus (Figure 5). The core barrel was mounted to an extruding disk and stabilizer disk on a threaded rod, then spacer plates of 1cm thickness were inserted between the stabilizer and an adjuster disk. Water was siphoned off and collected from the top of the core sample. To collect each sample, a spacer plate was removed and the core was hammered to expose 1cm of sediment in the extruding funnel, where it was scraped into a 50mL Falcon tube.



Figure 5. Example of a sediment core extrusion apparatus. 1 cm spacers are used to ensure collection of equal sediment samples. (Image courtesy of Aquatic Research Instruments)

Seaweed samples were stored frozen, then thawed and rinsed thoroughly with milliQ. Three samples each of tips, blades, and vesicles and one of the holdfast were dissected from each seaweed specimen.

Both sediment and seaweed samples were dried overnight at 60 °C for 48h. Approximately 10-20 g for each sediment sample and 1-5 g of each seaweed sample was finely powdered (~100 µm) in an agate mortar grinder.

5040' Tg'vgiui''

Rhenium abundances were first analyzed by inductively coupled plasma mass spectrometry (ICP-MS) in order to determine whether and which samples were enriched

enough to run on the more precise thermal ionization mass spectrometer (TIMS). Sample preparation for ICP-MS analysis involved aqua regia digestion, isotope dilution, and solvent extraction. For further background on isotope dilution, see section 3.5. First, approximately 0.1g of each sample was spiked with a mixture of a known ratio of stable isotope. Each sample was digested in an aqua regia mixture of 3mL HCl and 6mL HNO₃. Samples were inverted and left to digest at 120 °C for >18h. Cooled samples were centrifuged 3 minutes each and aqua regia was separated to dry at 120 °C for >18h again.

NaOH-C₃H₆O solvent extraction was used to isolate Re from the digested samples. 5mL of 5N NaOH solution and 5mL acetone were added to dried samples, agitated, and centrifuged for 3 minutes each. Re-bearing acetone is pipetted off and evaporated at 60 °C for ~18h. Dried Re mixtures were then brought up in 4mL of 0.8M HNO₃ and transferred to centrifuge tubes for Re abundance and composition analysis on the ICP-MS. Results were spike and blank-calibrated.

500' Ectku'wdg'ej go km{"cpf"eqmwo p"ej tqo cvqi tcrj {"

Thermal ionization mass spectrometry (TIMS) was used to obtain precise Re and Os abundance and isotopic compositions for select FOAM sediments and Re abundances for select seaweed samples. Sediment samples were selected evenly spread throughout the FOAM core and seaweed samples were selected representatively across specimens. Some samples were not tested as analysis was interrupted due to COVID-19.

This study used Carius tube Cr^{VI}O₃-- 4N H₂SO₄ digestion for sediment samples to preferentially isolate hydrogenous Re and Os from each sample and limit detrital components (Rooney et al. 2011, Selby and Creaser 2003). Inverse aqua regia (1:2 ratio

of HCl:HNO₃) was used for seaweed samples. Samples were prepared by loading ~0.8g into Carius tubes and spiking with a known concentration of ¹⁸⁵Re-¹⁹⁰Os tracer solution and acid medium (8 mL of 0.25 g/g Cr^{VI}O₃-- 4N H₂SO₄ for FOAM sediments; 9 mL of 1:2 mix of 11N HCl: 15.5N HNO₃ for seaweed samples). Carius tubes were frozen in dry ice and sealed using a torch to weld tubes shut. Sample, spike, and acid mixture was then heated at ~200°C for 48h. Carius tubes were re-frozen and opened using heat and gaseous pressure to shatter the glass. CHCl₃ solvent extraction into HBr was used to isolate Os from the acid medium. 3.5mL of chloroform was transferred to each carius tube, the mixture was agitated, and the chloroform was pipetted into 3mL 9N HBr. Os-bearing HBr was transferred to watch glasses flushed with 6N HCl and evaporated at ~80 . To prepare for analysis on the TIMS, Os was isolated using micro-distillation with CrO₃-H₂SO₄.

Re was isolated using NaOH-C₃H₆O solvent extraction and anion chromatography. Following Os solvent extraction, 1 mL of acid and sample mixture was dried down overnight and stirred with 15mL 5N NaOH solution cleaned with acetone. Fresh acetone was added and mixture was vortexed. 1mL of 6N HCl was added and fluxed on the hot plate for 30 minutes. Acetone was isolated and evaporated for column anion chromatography. 4mL of .2N HNO₃ was added and mixture was loaded into columns, which were then rinsed with .2N HNO₃ four times and .2N HCl twice before washing with 6N HNO₃. A final 4mL of 6N HNO₃ is added before the collected sample is dried down for Re analysis on the TIMS.

5060 Vj gt o cn'kqpk' c'kqp"o cuu'ur gev' qo gt { "

Re and Os abundance and Os isotopic composition was determined using the TIMS in the Yale Metal Geochemistry Center by PI Alan Rooney and graduate students. Samples were loaded on an evaporation filament and ionized on the ionization filament. Re and Os isotope compositions were obtained from Faraday cups and secondary electron multipliers. Uncertainties were determined by errors in Re and Os TIMS measurements, blank abundances and isotope compositions, and spike calibrations.

5070 "Kaqqr g'f kwwkqp"o cuu'ur gest qo gvt { "

Isotope dilution analysis is an important method for quantifying the abundance of distinct elemental isotopes in a sample using mass spectrometry, because these machines measure isotopic ratios. Concentrations can be calculated from these ratios if there is a known tracer, or spike, added to the sample. Isotope dilution typically uses an isotope of the element to be measured to eliminate the influence of chemical behavior in measurements (Becker 2012). This is often an artificial isotope (for example, ^{205}Pb for U-Pb analysis) or an isotopically enriched mixed tracer solution of a known ratio (for example, the mixture of ^{185}Re - ^{190}Os used in this study). Mass spectrometer results return the mixture isotopic ratio, so the ratio of the sample and isotopic and elemental abundances can be calculated, as in the sample formula below.

$$(^{187}\text{Os})_{\text{mix}} = (^{187}\text{Os})_{\text{sample}} + (^{187}\text{Os})_{\text{spike}}$$

$$(^{190}\text{Os})_{\text{mix}} = (^{190}\text{Os})_{\text{sample}} + (^{190}\text{Os})_{\text{spike}}$$

$$\left(\frac{^{187}\text{Os}}{^{190}\text{Os}}\right)_{\text{ok}} = \left(\frac{^{187}\text{Os}}{^{190}\text{Os}}\right)_{\text{ucorrg}} + \left(\frac{^{187}\text{Os}}{^{190}\text{Os}}\right)_{\text{urkng}}$$

$$\left(\frac{^{187}\text{Os}}{^{190}\text{Os}}\right)_{\text{ucorrg}} = \left(\frac{\left(\frac{^{187}\text{Os}}{^{190}\text{Os}}\right)_{\text{ok}} - \left(\frac{^{187}\text{Os}}{^{190}\text{Os}}\right)_{\text{urkng}}}{\left(\frac{^{187}\text{Os}}{^{190}\text{Os}}\right)_{\text{ucorrg}} - \left(\frac{^{187}\text{Os}}{^{190}\text{Os}}\right)_{\text{urkng}}}\right) * \frac{\text{urkng y gki j v}}{\text{ucorrg y gki j v}} * \left(\frac{^{190}\text{Os}}{^{187}\text{Os}}\right)_{\text{urkng}}$$

4. Results

6080 HQCO "Eqtg"

6080 Tj gplkw "cpf "Quo kw "cdwpcpegu"

Rhenium and osmium elemental abundances of all sediment samples analyzed from the FOAM core range from 1.3 to 4.38 ppb for Re, and 34.4 to 44.9 ppt for Os (Table 1).

6080 Quo kw "kqqr g"^{187:9}Qu¹⁸⁸: Qu+eqo rqukkqpu"

FOAM core records relatively stable ¹⁸⁷Os/¹⁸⁸Os compositions (1.05 ± .11, 1.8 SD, n=8) throughout the core (Figure 6). Isotopic compositions for all sediment samples analyzed in the FOAM core are provided in Table 1.

AMWJZ Ü

?Z M X 5y ZjZk Zl {MIM X'byn{nub/Vnk unyq}bnl 'XMIM Lnx" 5° 2 'yZXtk Zl {'VhxZ' XMIM

Zu{a	?Z	5y	ÜäY5y	Üäa?Zµ	Üäa5yµ	xan	5yb					
žk Ä	žuuUÄ ü	žuu{Ä ü	žuu{Ä ü	Üäa5y ü	Üäa5y ü							
ÜÜ	ßäpā	ÜÜp	ßÜÜ	ÜY	Üßā	ÜÜ	āāÜp	āā	ÜÜāā	ÜÜÜ	Üāāp	ÜÜā
ÜY	Üp	ÜÜ	ßßß	ÜY	ÜYā	ÜÜ	Üāāp	YÜ	ÜÜāā	ÜÜÜY	Üāāß	ÜÜā
ā1ā	pY	ÜÜ	ßßā	ÜY	Üāā	ÜÜ	pāāÜ	pY	Üāāā	ÜÜÜā	ÜāÜā	Üāā
ā1ā	Üāp	ÜÜÜ	pāā	ÜY	Üpā	ÜÜ	YpYā	Y	ÜÜßß	ÜÜÜ	Üāā	ÜÜß
Üā1Üā	pY	ÜÜ	ßÜā	ÜY	ÜāY	ÜÜ	ßÜāp	pā	Üāāā	ÜÜÜā	Üāāß	Üāā
Üā1Üā	pY	ÜÜ	pāÜ	ÜY	Üßß	ÜÜ	ßßÜp	pā	ÜÜāß	ÜÜÜ	ÜāÜß	ÜÜā
Yß1Yā	pÜā	ÜÜÜ	pā	ÜY	Üß	ÜÜ	ßßāÜ	ßÜ	ÜÜpā	ÜÜÜÜ	ÜāāY	ÜÜß
Yā1Yā	pÜā	ÜÜÜ	pāā	ÜY	Üpā	ÜÜ	ßßYā	ß	ÜÜāY	ÜÜÜY	Üāāß	ÜÜā

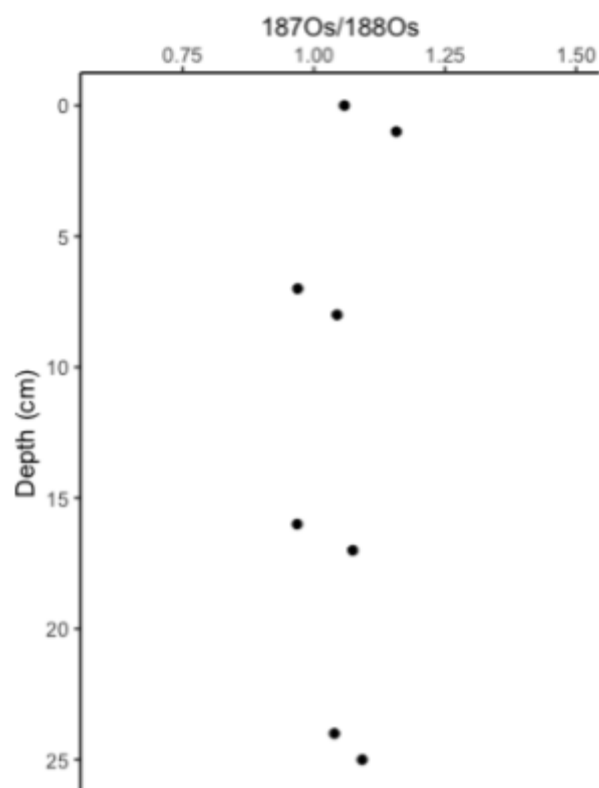


Figure 6. Depth profile of $^{187}\text{Os}/^{188}\text{Os}$ isotopic composition of the FOAM sediment core from the Long Island Sound.

600 *Ocetq/cni cg'Tg'cdwpcf cpegu'*

Due to COVID-19 complications, only select seaweed specimens and samples were analyzed and only for Re abundances (Table 2). The table also outlines the Os isotopic abundance and composition analysis that this study sought to complete and may be included in future work.

Re elemental abundances for all seaweed samples in this study range from 12.4 to 75.9 ppb. Seaweed from the FOAM site range from 17.3 to 75.9 ppb and from

Svalbard 12.6 to 50.0 ppb (Figure 7). Blades range from 12.6 to 27.1 ppb and tips from 12.4 to 75.9 ppb."

ANWjZ Ý		
?Z'ZjZk ZI {MjMw XMjVZy_nx'yZMj ZZx'yMk ujZy ^a		
	?Z'	5y'
	gjuUA'	gju{A'
UäY5y'		
	gju{A'	Uäa5yµUäa5y'
	ü'	5ybMj{'
Svalbard (<i>Ascophyllum nodosum</i>)		
<u>@uZVtk ZI Ý'</u>		
Abuy'	ÜY ^a B'	Ü ^a Ü'
ŁjMkZy'	ÜY ^a a'	Ü ^a Ü'
<u>@uZVtk ZI P'</u>		
Abuy'	äÜ ^a Ü'	Ü ^a Ü'
ŁjMkZy'	Yä ^a Ü'	Ü ^a Ü'
Long Island Sound (<i>Fucus Vesiculosus</i>)		
<u>@uZVtk ZI Ü'</u>		
Abuy'	ää ^a a'	Ü ^a Y'
<u>@uZVtk ZI Ý'</u>		
Abuy'	Pä ^a Ü'	Ü ^a Ü'
ŁjMkZy'	Üä ^a P'	Ü ^a Ü'

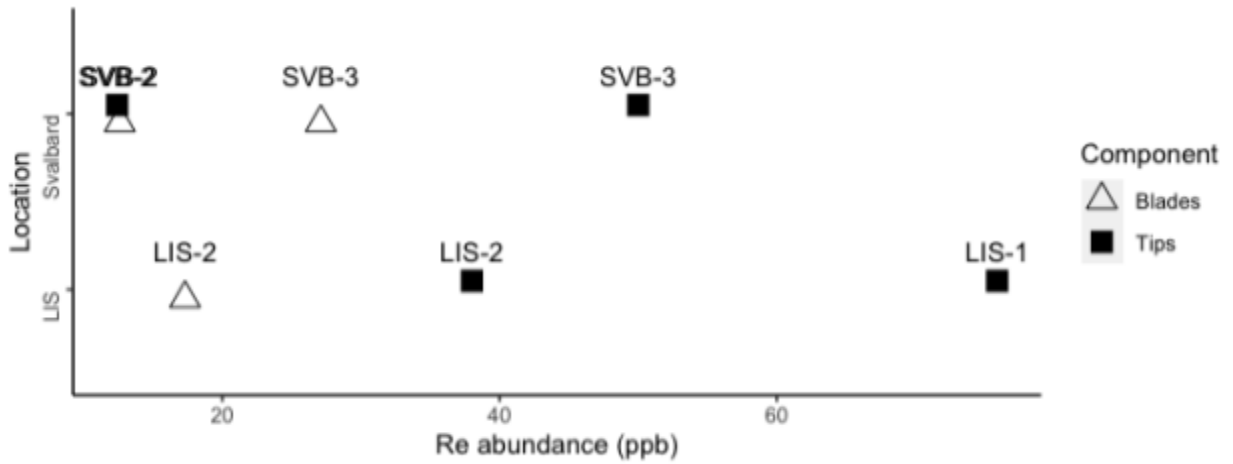


Figure 7. Re abundances for macro-algae samples plotted by study site and seaweed component.

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5. Discussion

5.1. *Dkqrqi kecn'wrcng"qhTg"cpf 'Qu'*

All samples of macro-algae from both study sites concentrate Re (12.4 - 75.9 ppb) in significantly higher abundances than the FOAM sediment core (1.3 - 4.48 ppb) (Table 1). The biological uptake of Re seems to differ between structures, with blades averaging 19.0 ppb (SD 7.4) and tips averaging 44.1 ppb but with greater variation (SD 26.4). Previous studies have indicated that Re uptake is associated with seaweed growth and therefore accumulation in the tips is seasonally influenced (Racionero-Gomez 2016). The high abundance of Re supports the hypothesis that macro-algae is concentrating the Re in the water column.

We would expect Os abundances to be significantly higher in the macro-algae samples relative to the sediments as well, based on the 2016 work by Racionero-Gomez et al. on *Hwewu'xgukewrquku*. "The $^{187}\text{Os}/^{188}\text{Os}$ composition of each sample is expected to have accurately captured that of its environment. If the $^{187}\text{Os}/^{188}\text{Os}$ isotopic signature of Long Island Sound macro-algae reflects that of the surface sediments from the FOAM site (near the canonical open-ocean figure of 1.06), this would provide strong evidence that both seaweed and sediment are capturing snapshots of seawater isotopic composition. It would also indicate that

biological inputs comprise a significant portion of the hydrogenous components of the sedimentary record of Os composition.

5.2 *Tgukf gpeg'vko g'qhl'Qu'lp'vj g'qegcp"*

The marine residence time of Os is canonically cited as $\sim 10^4$ years, but recent studies have indicated that its isotopic composition can fluctuate more rapidly in certain environments and are largely dependent on setting (Paquay and Ravizza 2012). This is particularly true in coastal environments influenced by oceanic currents and concentrated influx of different weathering inputs (Rooney et al. 2016).

$^{187}\text{Os}/^{188}\text{Os}$ isotopic compositions in the FOAM core are relatively stable at the canonical global ocean value of 1.06. This is consistent with the interpretation of this site as nearly open-ocean. However, variation in the FOAM core data is visible in Figure 6, at a time scale on the order of $<10^3$ years. Further analysis should be done on the remainder of the FOAM core, but this seems to indicate in estuarine environments like the Long Island Sound, Os residence time may be shorter than the global open ocean.

We would have expected the $^{187}\text{Os}/^{188}\text{Os}$ composition of Svalbard macro-algae samples to reflect the proximity to sources of weathering bedrock, with greater variation. This would have further supported the conclusion that seawater Os composition is determined locally in near-field environments.

6. Conclusions

The Os isotopic compositions and Re abundances presented here show the important role that biological sources have in incorporating these elements in the stratigraphic record. Future work on the isotopic composition of macro-algae is needed to further our understanding of how the $^{187}\text{Os}/^{188}\text{Os}$ geochronometer is recorded in the hydrogenous portion of ocean sediments. Additionally, this study indicates that variation in the Os composition of seawater can change on timescales shorter than the canonical $\sim 10^4$ years.

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References

- Becker, J. S., 2012. "Isotope Dilution Techniques." *J. Geophys. Res.* **117**, G04001. doi:10.1029/2011JD016441
- Esser, B. K., Turekian, K.K., 1993. Anthropogenic osmium in coastal deposits. *Environmental Science Technology* **27**, 2179-2724.
- Gay, P. S., O'Donnell J., Edwards, C.A., 2004. Exchange between Long Island Sound and adjacent waters. *American Geophysical Union*.
- Ingolfsson, O. Outline of the Physical Geography and Geology of Svalbard. University of Iceland.
- Krishnaswami, S., Monaghan, M.C., Westrich, J.T., Bennett, J.T., Turekian, K.K., 1984. Chronologies of sedimentary processes in sediments of the FOAM site, Long Island Sound, Connecticut. *American Journal of Science* **284**, 706-733.
- Oxburgh, R., 2001. Residence time of osmium in the oceans. *Geochem. Geophys.*
- Paquay, F.S., Ravizza, G., 2012. Heterogeneous seawater $^{187}\text{Os}/^{188}\text{Os}$ during the Late Pleistocene glaciations. *Earth Planet. Sci. Lett.* **349**, 126-138.
- Racionero-Gomez, B., Sproson, A.D., Selby, D., Gannoun, A., Grocke, D.R., Greenwell, H.C., Burton, K.W. 2016. Osmium uptake, distribution, and $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ compositions in Phaeophyceae macroalgae, *Fucus vesiculosus*: Implications for determining the $^{187}\text{Os}/^{188}\text{Os}$ composition of seawater. *Geochimica et Cosmochimica Acta* **199**, 48-57.

- Rooney, A.D., Selby, D., Lloyd, J.M., Roberts, D.H., Luckge, A., Sageman, B.B., Prouty, N.G. 2016. Tracking millennial-scale Holocene glacial advance and retreat using osmium isotopes: Insights from the Greenland ice sheet, *Quaternary Science Reviews* 138, 49-61.
- Rooney, A.D., Chew, D.M., Selby, D., 2011. Re-Os geochronology of the Neoproterozoic-Cambrian Dalradian Supergroup of Scotland and Ireland: implications for neoproterozoic stratigraphy, glaciations and Re-Os systematics. *Precambrian Res* 185, 202-214.
- Selby, D., Creaser, R.A., 2003. Re-Os geochronology of organic rich sediments: an evaluation of organic matter analysis methods. *Chemical Geology* 200, 225–240.
- Stein, H., Hannah, J. 2014. Rhenium–Osmium Geochronology: Sulfides, Shales, Oils, and Mantle. *Encyclopedia of Scientific Dating Methods*.
- White, N., Hill, J.M. 2008. *Ascophyllum nodosum*. Plymouth: Marine Biological Association of the U.K.
- White, N. 2008. *Fucus vesiculosus*. Plymouth: Marine-Biological Association of the U.K.