# Marine macroalgae are an overlooked sink of silicon in coastal systems

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## Introduction

Across the marine landscape, from estuaries to the open ocean, biota take up silicon (Si) as monosilicic acid and deposit it into their tissues as biogenic silica (BSi). Along the coast, vegetated ecosystems, such as salt marshes and mangroves, sequester a significant amount of Si in their tissues and likely help regulate the availability of Si in surrounding waters (Carey & Fulweiler, 2014; Elizondo *et al.*, 2021). Si is also accumulated by sponges, euglyphid amoebae, radiolarians, silicoflagellates, and choanoflagellates, as well as a few coccolithophores, Prasinophyceae, and picocyanobacteria (Raven & Giordano, 2009; Gadd & Raven, 2010; Baines *et al.*, 2012). The dominant driver of coastal (and open ocean) Si cycling, however, is generally thought to be diatoms. These siliceous phytoplankton require Si on a 1 : 1 molar ratio with nitrogen (N). Diatoms are responsible for 40–50% of global marine primary production (Field *et al.*, 1998; Rousseaux & Gregg, 2013) and form the base

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of the marine food web in many parts of the ocean, especially coastal temperate regions (Irigoien *et al.*, 2002).

Macroalgae are also important primary producers, particularly in shallow coastal marine ecosystems, with global net primary production of 80–210 Tmol C yr$^{-1}$ (Raven, 2018). Macroalgae act as a food source for grazers (Horne *et al.*, 1994) and play a large role in altering the cycling of nutrients, such as N and phosphorus (P) (Hersh, 1995). Many estuaries have experienced a shift towards macroalgae as the dominant group of primary producers over the past several decades (Valiela *et al.*, 1992; Hauxwell *et al.*, 2001; Potter *et al.*, 2021). This is due to the ability of macroalgae to thrive in nutrient-rich systems, displacing other primary producers by way of rapid uptake of N and P and shading of photosynthetic organisms below (e.g. the seagrass *Zostera*; Valiela *et al.*, 1992, 1997; Peckol *et al.*, 1994).

The role of macroalgae on Si availability, however, is largely unconstrained, with only a few published studies reporting BSi concentrations. Work on freshwater macrophytes found BSi concentrations ranged from 0.2% to 2.8% (by dry weight), and the percentage of BSi was positively correlated to water flow (Schoelynck *et al.*, 2010, 2012). Research from four decades ago on freshwater macroalgae demonstrated more rapid growth in *Cladophora glomerata* when Si was added to the growth medium (Moore & Traquair, 1976). The stipe of *Ecklonia cava* was reported to contain BSi concentrations of 13.35 lg g$^{-1}$ dry mass (0.0013% BSi), and the tissue of *Delisea fimbriaia* contained 1530 lg g$^{-1}$ dry mass (0.15% BSi) (Fu *et al.*, 2000). More recently, BSi concentrations of the sporophytes of kelp, *Saccharian japonica*, were found to vary by location on the blade (Mizuta & Yasui, 2012) and to increase when *S. japonica* experienced various stresses (Mizuta *et al.*, 2021). Similarly, BSi concentrations of *Pyropia yezoensis* increased when exposed to increased temperature and reached a concentration of 30% BSi (Le *et al.*, 2019).

We hypothesized that marine macroalgae may contain significant amounts of Si in their biomass and thus could impact the Si cycle of coastal ecosystems. To determine the extent to which marine macroalgae are a reservoir of Si, we quantified BSi concentrations from 12 macroalgae genera from two temperate estuaries (Narragansett Bay, Rhode Island, and Waquoit Bay, Massachusetts, USA), and from a subset of samples we measured macroalgae percentage carbon (C). Finally, from one of the estuaries, we used macroalgae d$^{13}$C values, which can be used as a proxy for identifying $CO_2$ or bicarbonate source in photosynthesis, to infer the presence/absence of C concentration mechanisms (Raven *et al.*, 2002) and as an indicator of productivity (Oczkowski *et al.*, 2010). We then examined the relationship between BSi concentrations and macroalgae d$^{13}$C to better understand mechanisms driving BSi uptake.

## Materials and Methods

### Macroalgae sampling

We collected macroalgae samples from Waquoit Bay (MA, USA) from the surface water using a sampling net, or from the bottom water using a Ponar benthic grab (523 cm$^2$). Three sites were sampled (Child's River Estuary, Metoxit Point, and Sage Lot Pond) on

four separate occasions (September 2015, October 2015, and twice in June 2016). We also collected macroalgae samples by hand from 19 sites in Narragansett Bay (RI, USA) on one occasion (September 2015). Narragansett Bay samples were collected from just below the water surface at the bases of lighthouses and rocky outcrops during low tide. All samples were stored in plastic containers and bags in the dark until return to the laboratory, where they were then frozen until analysis.

### Biogenic silica, carbon : nitrogen, and d13C analysis

Before BSi analysis, the macroalgae samples were separated by genus and, where possible, to species. Next, they were rinsed with deionized water and gently brushed to remove any visible epiphytes. Samples were then placed in ethanol-cleaned aluminum tins, and dried at 60°C for a minimum of 72 h. Following drying, the sample was ground and homogenized using a Wig-L-Bug™ (Fisher Scientific, Waltham, MA, USA).

We quantified BSi concentrations in the ground macroalgae samples using the wet alkaline extraction technique in 1% sodium carbonate solution wet alkaline digestion method (DeMaster, 1981; Conley & Schelske, 2002). Briefly, 30 mg of ground sample (weighed to a precision of 0.1 mg) was processed in flat-bottomed polyethylene bottles. We used a Seal AA3 (Seal Analytical Ltd, Mequon, WI, USA) flow injection autoanalyzer to determine dissolved silica ($SiO_2$) concentrations of the digestate using the molybdenum blue colorimetric method (Strickland & Parsons, 1968). We used sodium hexafluorosilicate as the Si standard (Strickland & Parsons, 1968) as well as Hach external standards, to ensure accuracy. All standards were within 4% of expected value, and minimum detection limits during analysis were 0.030 $\mu$mol $l^{-1}$. We then converted dissolved $SiO_2$ concentrations of the digestate back to macroalgae percentage BSi by mass (Conley & Schelske, 2002). Finally, when reporting molar ratios of C : Si, we converted our BSi values to Si by multiplying by 0.47, the mass fraction of Si in the $SiO_2$ molecule (Elizondo *et al.*, 2021).

A subset of the Waquoit Bay macroalgae samples were analyzed for percentage C and N using standard methods (Dalsgaard *et al.*, 2000) and a Eurovector CHN elemental analyzer at the Boston University Stable Isotopes Lab (Boston, MA, USA). All of the Narragansett Bay samples were analyzed for percent C and N and d13C on a Carlo-Erba NA 1500 Series II elemental analyzer interfaced with a Micromass Optima mass spectrometer (Oczkowski *et al.*, 2018).

### Data analysis

All statistical analyses were conducted in R v.3.6.0 (R Development Team, 2014). We considered the results of statistical tests to be significant when $P$  0.05. Figures were made using GGPLOT2 (Wickham, 2016) and COWPLOT (Wilke, 2019). We determined data distributions using the FITDISTRPLUS package (Marie *et al.*, 2015) by comparing whether the data were best described by a normal, lognormal, or gamma distribution. Percentage BSi data were best described by a lognormal distribution, and C : Si best fit a gamma distribution. All measured d13C values were negative, so we mirrored them around zero to test their distribution, which we found to be normal.

To compare the relationship of macroalgae percentage BSi across phyla and genera, we used a generalized linear mixed model (GLMM) approach via the LME4 package (Bates *et al.*, 2015). In each GLMM, we set phylum or genus as a fixed effect and the estuary as a random effect. The percentage BSi data were lognormally distributed, so we first applied a log transformation to the percentage BSi data before constructing the model, but the resulting models had heteroscedastic residuals. We remade the model using a gamma family with a log-link, after which the residual distribution improved (Zuur *et al.*, 2009). Following model construction, we compared groups using pairwise least-square means tests using the EMMEANS package (Lenth, 2018). We tested for relationships between percentage C and BSi concentrations and between log-transformed BSi concentrations and $d^{13}C$ using linear regressions. We tested for correlations between percentage BSi or percentage C with latitude using Spearman correlation.

## Results

Individual macroalgae samples varied widely in BSi concentration from a low of 0.13% in *Laminaria* to a high of 39.4% in *Polysiphonia* (Fig. 1). At the phylum level, Rhodophyta had significantly ($P < 0.0001$) higher BSi concentrations than Ochrophyta and Chlorophyta, and Chlorophyta had significantly ($P < 0.0001$) higher BSi concentrations than Ochrophyta. The high Rhodophyta BSi concentrations were primarily driven by the genera *Cystoclonium* and *Polysiphonia*, which exhibited BSi concentrations almost 10 times that of the other macroalgae samples, regardless of phylum (Table 1). Genera BSi concentrations within Chlorophyta and Ochrophyta were not significantly different from each other. Genera within Rhodophyta were statistically different from each other (Table 2).

BSi concentrations were significantly negatively related to percentage C ($P < 0.0001$, $R^2 = 0.48$; Fig. 2a). There was also a significant negative relationship between log-transformed macroalgae BSi concentrations and $d^{13}C$ ($P < 0.01$, $R^2 = 0.42$; Fig. 2b), where $d^{13}C$ was more depleted as BSi concentrations increased.

## Discussion

BSi concentrations vary widely in Si-requiring marine biota. For example, even within a single diatom species, BSi concentrations can vary by an order of magnitude (Taylor, 1985; Claquin *et al.*, 2002). Similarly, BSi concentrations in these macroalgae also varied widely across genera (Fig. 1). In general, the BSi concentrations (4.2 ± 0.84%, mean ± SE) in macroalgae exceeded or were on par with values reported for salt marsh grasses collected in Narragansett Bay and other nearby estuaries (*Spartina patens*: 0.63 ± 0.38% BSi by weight; *Spartina alterniflora*: 0.57 ± 0.24% BSi by weight; Carey & Fulweiler, 2014). These macroalgae BSi concentrations are also generally higher than those reported for leaves of seagrasses (e.g. 0.06–0.7%; Vonk *et al.*, 2018). Overall, there was low variability within phylum, except for Rhodophyta, where BSi concentrations varied widely. The high variability of BSi concentrations may be driven by different responses of macroalgae to environmental conditions and/or stressors.

The siliceous wall in diatoms confers a range of benefits, including providing structural support for their large protoplast (Raven & Waite, 2004; Finkel & Kotrc, 2010), increasing nutrient uptake (Mitchell *et al.*, 2013), aiding light harvest (Romann *et al.*, 2015), protection from ultraviolet radiation (Aguirre *et al.*, 2018), reducing herbivory (Panči'c *et al.*, 2019), and possibly limiting viral infection (Raven & Waite, 2004). The large variations in diatom Si concentrations are thought to be driven in part by environmental conditions, such as light and nutrient availability (Brzezinski, 1985) as well as grazing pressure (Panči'c *et al.*, 2019). A recent study by Panči'c *et al.* (2019) reported that the cell wall of diatoms thickened under copepod grazing pressure, and that $SiO_2$ deposition decreased with increasing diatom growth rates. Their results suggest diatoms use Si as a defense but that this defense comes at a cost. Macroalgae may also be taking up Si for similar reasons, and potentially they, too, may need to sacrifice growth for defense or vice versa – defense for growth.

We can examine some of these factors a bit more closely for the macroalgae samples from Narragansett Bay, which were collected from sites along a gradient of potential stressors. Narragansett Bay is orientated in a roughly north–south position with lower salinity, higher inorganic nutrient concentrations, including dissolved $SiO_2$, and higher rates of primary production in the northern reaches of the bay, where light is also typically more limited (Oviatt *et al.*, 2002; Smayda & Borkman, 2008; Nixon *et al.*, 2009). Whereas macroalgae BSi concentrations did not vary by location within Narragansett Bay as a whole, BSi concentrations for Rhodophyta alone significantly decreased ($r = -0.47$, $P = 0.034$), whereas percentage C increased ($r = 0.62$, $P = 0.008$) along this north–south gradient. That is, the Rhodophyta samples collected in northern Narragansett Bay incorporated more Si into their biomass and less C. Overall, we found that BSi concentrations increase as macroalgae percentage C decreases, suggesting that macroalgae may substitute Si for C (Fig. 2a). This relationship was again driven by macroalgae in the phylum Rhodophyta, whereas samples for Chlorophyta and Ochrophyta tended to vary less in terms of BSi concentration and percentage C. An inverse relationship between C and BSi concentration has been reported for a variety of flowering plant species – for example, *Phragmites australis* (Schaller *et al.*, 2012) and *Triticum aestivum* (Neu *et al.*, 2017) – as well as for grassland ecosystems (Quigley *et al.*, 2020). Additionally, Schoelynck *et al.* (2010) found a negative relationship between cellulose and BSi concentrations for freshwater macrophytes. Incorporating Si is an energetically cheaper mechanism for structural support (Raven, 1983) while also providing additional benefits. These findings suggest that certain macroalgae, primarily in the phylum Rhodophyta, may take up Si in response to *in situ* availability and/or environmental stressors, similar to what is observed for diatoms. The inverse relationship between BSi concentration and percentage C may also prove to be useful for scaling. That is, percentage C data are more widely available for macroalgae than BSi concentration. If this relationship holds for more species and more locations then we may be able to use the more abundant percentage C data to predict how much Si is taken up across space and time.

We also observed a negative relationship between $d^{13}C$ and BSi concentrations (Fig. 2b). These relationships described a substantial portion of the variance in $d^{13}C$, which can be used to help understand macroalgae photosynthetic pathways (Giordano *et al.*, 2005; Marconi *et al.*, 2011; Lovelock *et al.*, 2020) and environmental conditions influencing macroalgae growth (Dudley *et al.*, 2010). The $d^{13}C$ values reported here (−12.60& to

−23.54&) are well within the range reported for macroalgae (Maberly *et al.*, 1992; Raven *et al.*, 2005; Lovelock *et al.*, 2020). These values also suggest that inorganic C entry is driven by a combination of $CO_2$ diffusion directly to Rubisco and through the C-concentrating mechanisms. There is a clear pattern with phylum $d^{13}C$ and BSi concentrations (Fig. 2b). At this point we are uncertain what mechanism is driving the pattern between $d^{13}C$ and BSi concentration. Perhaps, it is simply a correlation with – as the well-worn phrase goes – no causation. Alternatively, it may provide insight into how and why macroalgae take up Si. The more negative $d^{13}C$ associated with higher BSi is consistent with a large fraction of the inorganic C being pumped into cells in the organism with C-concentrating mechanisms, or diffusive $CO_2$ entry, allowing discrimination against $d^{13}C$ by Rubisco. All other things being equal, that may indicate lower growth rates and hint at the tradeoffs of incorporating Si. However, we cannot at this time connect the $d^{13}C$ directly to BSi concentrations as the factors driving $d^{13}C$ signatures are upstream of allocation of photosynthate to growth or Si uptake.

Finally, uptake of Si by macroalgae may help promote Si limitation in estuaries, especially if they are actively sequestering it, and therefore competing with diatoms for Si. We can estimate the amount of Si taken up by macroalgae by using the C : Si ratio measured here and values reported in the literature for global macroalgae primary productivity. Annually, global macroalgae net primary production (and C uptake) ranges from 80 to 210 Tmol C $yr^{-1}$ (Raven, 2018). Scaling this by the mean macroalgae C : Si molar ratio measured in this study (295.6), we calculate an average global macroalgae uptake rate between 0.27 and 0.71 Tmol Si $yr^{-1}$. The maximum value accounts for almost 10% of the Si entering the ocean from rivers and over 40% of the annual uptake of Si by sponges (Tr'eguer *et al.*, 2021). This is likely a conservative estimate, as using the median C : Si molar ratio in this study (157.4) would increase global macroalgae uptake to between 0.5 and 1.33 Tmol Si $yr^{-1}$. In this case, the maximum value would account for 16% of the Si entering the ocean from rivers and almost 80% of the annual uptake of Si by sponges. Potentially, these values could be higher. For example, a recent environmental DNA study reported that Rhodophyta, the genera with the highest BSi concentrations in this study, were the dominant genera of macroalgae found in the world's oceans (Ortega *et al.*, 2019). Of course, our calculations are a rough approximation based on temperate macroalgae only. We anticipate the BSi concentrations may vary by geographic location, seasonality, and exposure to stress. Regardless, this study suggests marine macroalgae are a potentially important, yet largely ignored, sink of Si in marine ecosystems. This sink may be particularly important in systems that are heavily fertilized with inorganic N and P, where macroalgae come to dominate. Perhaps macroalgae Si uptake contributes to Si limitation in coastal systems, thereby exacerbating the negative impacts of eutrophication.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgements

## Data availability

All data are available via https://doi.org/10.6084/m9.figshare.15113139.v1.

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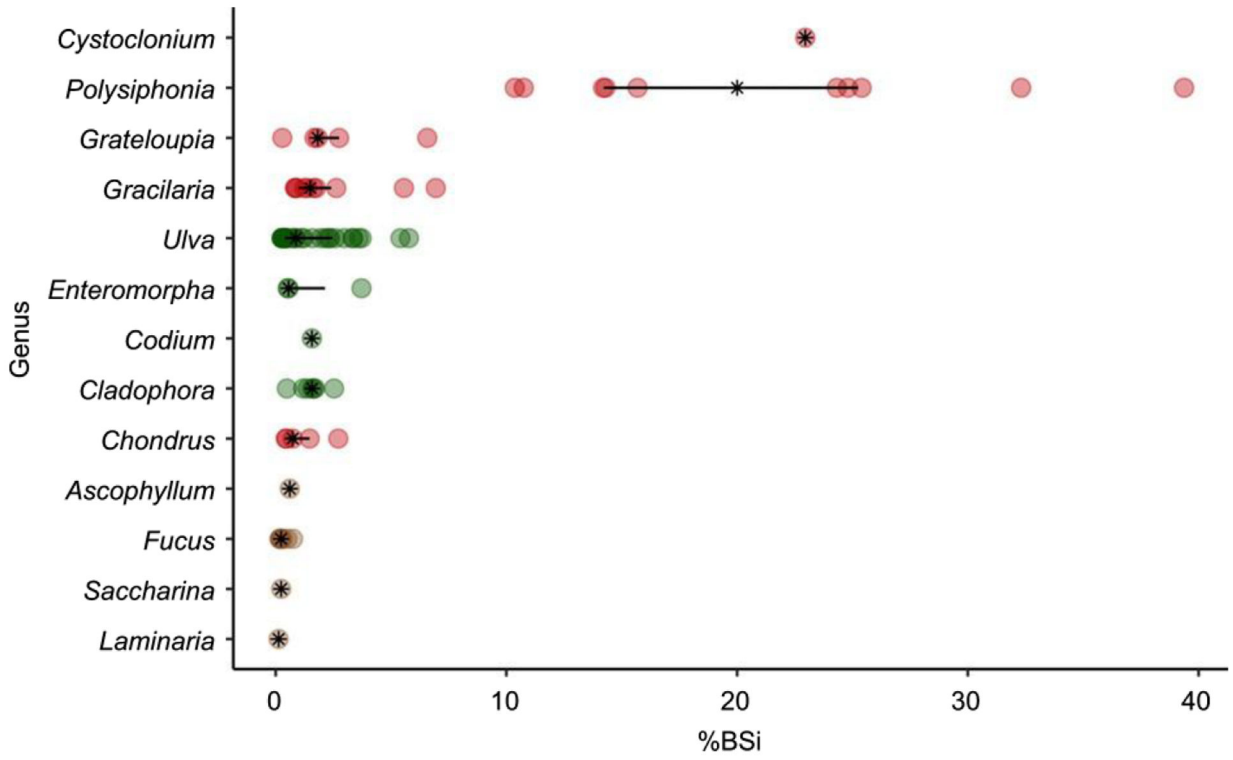
**Fig. 1.**
Median (black asterisk) and the interquartile range of biogenic silica (%BSi as $SiO_2$ per DW) concentrations of macroalgae by genus. Individual sample values are also shown as circles color coded by phylum (Chlorophyta, green; Ochrophyta, brown; Rhodoyphta, red).
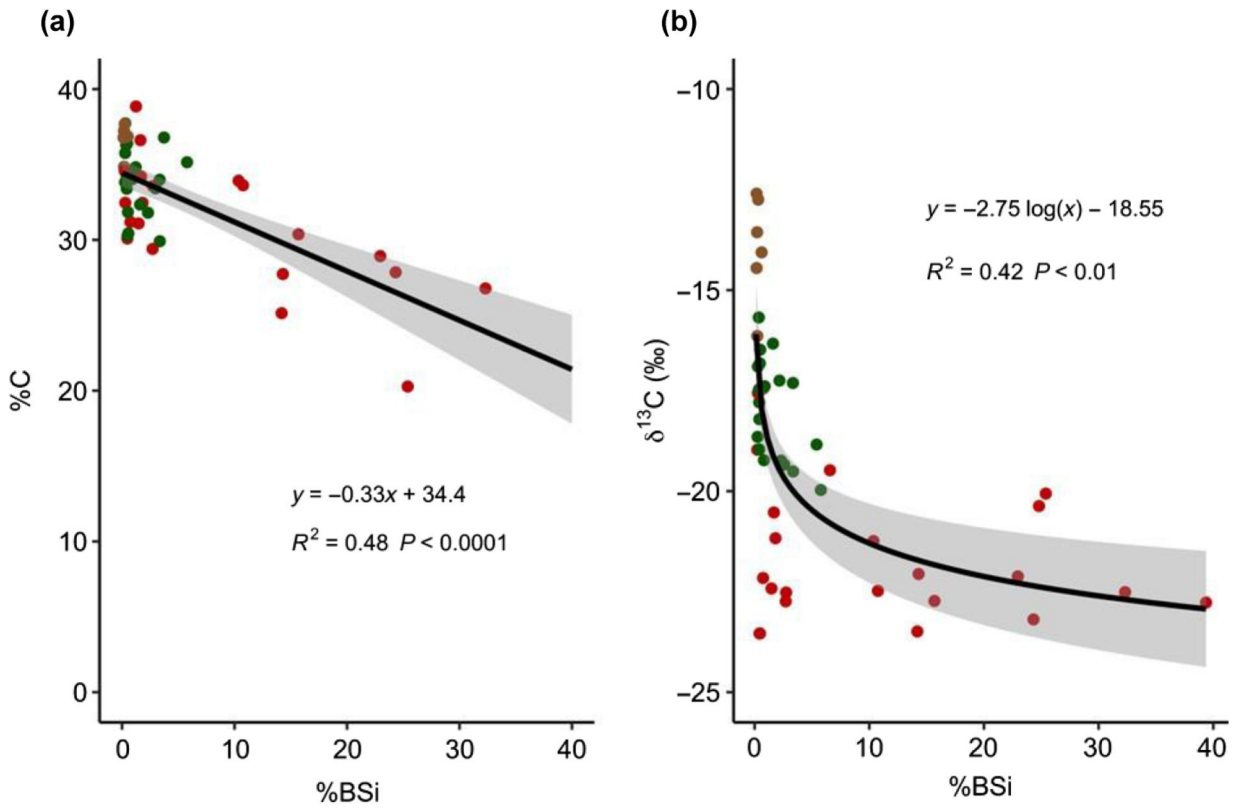
**(a)**



**(b)**

$$y = -0.33x + 34.4$$
$$R^2 = 0.48 \ P < 0.0001$$

$$y = -2.75 \log(x) - 18.55$$
$$R^2 = 0.42 \ P < 0.01$$

**Fig. 2.**
Relationship between (a) biogenic silica (%BSi as $SiO_2$ per DW) and percentage carbon (%C) content and (b) biogenic silica and $d^{13}C$ in macroalgae samples collected from Narragansett Bay (RI, USA). Samples are color coded by phylum (Chlorophyta, green; Ochrophyta, brown; Rhodophyta, red). The shaded area around the regression line is the 95% confidence interval.

**Table 1**

Mean (± SE) biogenic silica concentrations (%BSi as $SiO_2$ DW) in macroalgae from Narragansett Bay (RI, USA) and Waquoit Bay (MA, USA).

| Phylum | Genus | *n* | %BSi |
|---|---|---|---|
| Chlorophyta | *Cladophora* | 7 | 1.50 ± 0.23 |
| | *Codium* | 1 | 1.57 |
| | *Enteromorpha* | 3 | 1.60 ± 1.06 |
| | *Ulva* | 31 | 1.63 ± 0.28 |
| Ochrophyta | *Ascophyllum* | 1 | 0.61 |
| | *Fucus* | 7 | 0.34 ± 0.08 |
| | *Laminaria* | 1 | 0.13 |
| | *Saccharina* | 1 | 0.24 |
| Rhodophyta | *Chondrus* | 5 | 1.16 ± 0.43 |
| | *Cystoclonium* | 1 | 22.96 |
| | *Gracilaria* | 10 | 2.37 ± 0.68 |
| | *Grateloupia* | 5 | 2.62 ± 1.06 |
| | *Polysiphonia* | 10 | 21.15 ± 3.07 |

**Table 2**

*P*-values from least square mean comparisons of biogenic silica (%BSi as $SiO_2$ per dry wt) content of macroalgae genera.

| | Chondrus | Cladophora | Codium | Cystoclonium | Enteromorpha | Fucus | Gracilaria | Grateloupia | Laminaria | Polysiphonia | Saccharina | Ulva |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Ascophyllum* | 0.999 | 0.996 | 1.00 | 0.031 | 0.996 | 1.00 | 0.876 | 0.853 | 0.957 | <0.001 | 1.00 | 0.985 |
| *Chondrus* | | 1.00 | 1.00 | 0.015 | 1.00 | 0.179 | 0.874 | 0.883 | 0.237 | <0.001 | 0.757 | 0.999 |
| *Cladophora* | | | 1.00 | 0.033 | 1.00 | 0.011 | 0.990 | 0.988 | 0.089 | <0.001 | 0.492 | 1.00 |
| *Codium* | | | | 0.336 | 1.00 | 0.773 | 1.00 | 1.00 | 0.444 | 0.045 | 0.847 | 1.00 |
| *Cystoclonium* | | | | | 0.090 | <0.001 | 0.151 | 0.268 | <0.001 | 1.00 | 0.001 | 0.027 |
| *Enteromorpha* | | | | | | 0.111 | 1.00 | 1.00 | 0.137 | <0.001 | 1.00 | 1.00 |
| *Fucus* | | | | | | | <0.001 | <0.001 | 0.991 | <0.001 | 1.00 | <0.001 |
| *Gracilaria* | | | | | | | | 1.00 | 0.011 | <0.001 | 0.135 | 0.978 |
| *Grateloupia* | | | | | | | | | 0.012 | <0.001 | 0.136 | 0.984 |
| *Laminaria* | | | | | | | | | | <0.001 | 1.00 | 0.039 |
| *Polysiphonia* | | | | | | | | | | | <0.001 | <0.001 |
| *Saccharina* | | | | | | | | | | | | 0.330 |

Significant differences (*P* 0.05) are bolded. See Table 1 for mean BSi concentrations.