Supporting Information for:

Bio-mimicked silica architectures capture geometry, microstructure, and mechanical properties of marine diatoms.

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1. Relative-density calculation for diatom frustules (adapted from Aitken et al.[1])

We define the relative density of the diatom frustule as the ratio of material volume in the frustule, $V_{frustule}$, to volume in a monolithic shell of equal dimension, V_{solid}.

$$\rho_{relative} = \frac{V_{frustule}}{V_{solid}} = \frac{V_{cribrum}+V_{areolae}+V_{basal}+V_{rim}}{V_{solid}} \qquad \text{Eq. (S1)}$$

Where $V_{cribrum}$, $V_{areolae}$, and V_{basal} are the volume of the cribrum, areolae, and basal layers and V_{rim} is the volume of the raised foramen rim. Due to periodicity of the frustule, we start by considering a single hexagonal unit of the frustule as shown in Figure S2 and develop a general model for the relative density. Figures S2b-d show schematics of the projected area in each layer of the frustule. By defining the relative projected area as the ratio of projected area for a given layer *i*, A_i, and the solid area, A_{solid}, Eq. S1 can be re-written as:

$$\rho_{relative} = \frac{A_{cribrum}}{A_{solid}}\frac{w_{cribrum}}{w_{total}} + \frac{A_{areolae}}{A_{solid}}\frac{w_{areolae}}{w_{total}} + \frac{A_{basal}}{A_{solid}}\frac{w_{basal}}{w_{total}} + \frac{A_{rim}}{A_{solid}}\frac{w_{rim}}{w_{total}} \qquad \text{Eq. (S2)}$$

Where $w_{cribrum}$, $w_{areolae}$, and w_{basal} are the depth of the cribrum, areolae, and basal layers and w_{rim} is the thickness of the raised foramen rim. $w_{total} = w_{cribrum} + w_{areolae} + w_{basal} + \frac{1}{2}w_{rim}$ is the total depth of the beam.

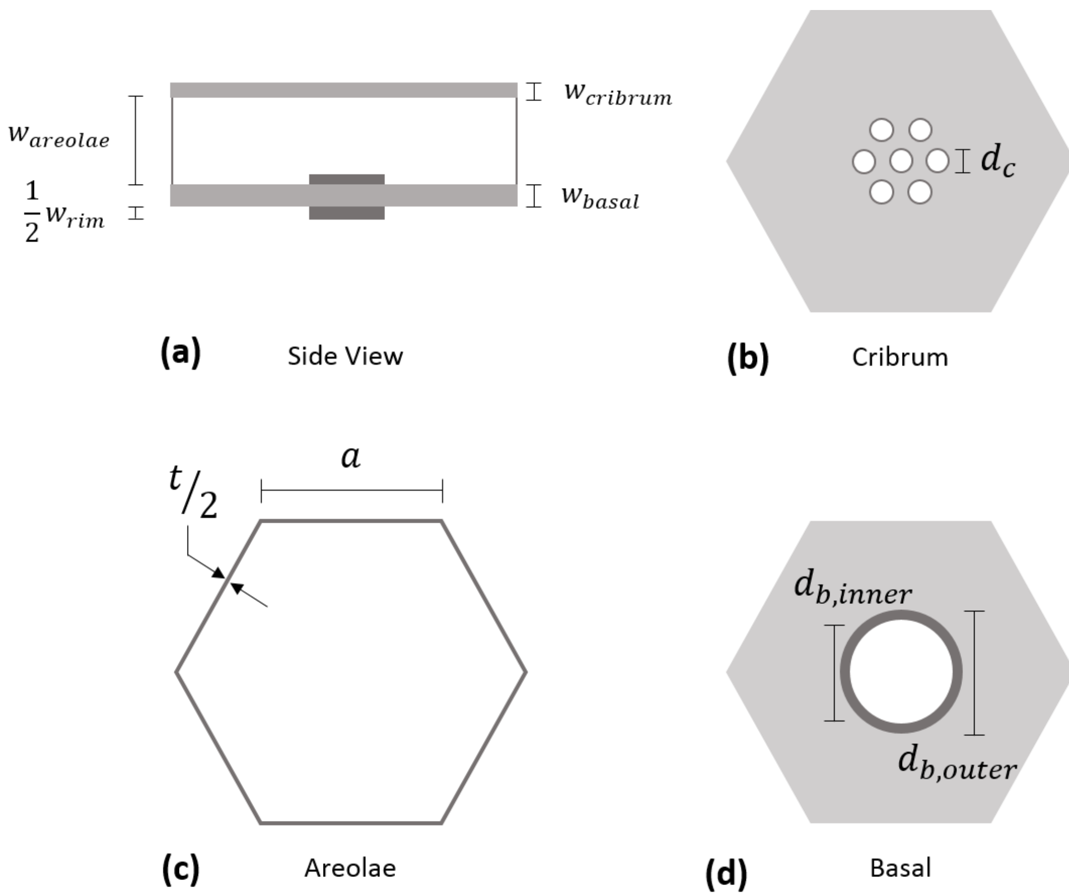

Figure S2: Schematic showing the hexagonal unit of frustule. (a) gives a cross-section of the frustule shell. (b), (c), (d) show top-down views of each layer of the frustule shell.

From the observed hexagonal arrangement of pores in the cribrum, we assume 7 cribrum pores per hexagonal unit. The projected area of the cribrum is then given:

$$A_{cribrum} = A_{solid} - \frac{7\pi}{4} d_c^2 \quad \text{Eq. (S3)}$$

Where d_c is the diameter of a cribrum pore. The total area of the walls that make up the areolae is:

$$A_{areolae} = A_{solid} - \frac{3\sqrt{3}}{2}\left(a - \frac{t}{\sqrt{3}}\right)^2 \quad \text{Eq. (S4)}$$

Where *a* and *t* are the length and thickness of the areolae wall. The area within the basal layer and area of the raised rim are:

$$A_{basal} = A_{solid} - \frac{\pi}{4} d_{b,inner}^2 \qquad \text{Eq. (S5)}$$

$$A_{rim} = \frac{\pi}{4}\left[d_{b,outer}^2 - d_{b,inner}^2\right] \qquad \text{Eq. (S6)}$$

Where $d_{b,inner}$ and $d_{b,outer}$ are the inner and diameter of the foramen rim. Noting that the solid area is simply the area of the hexagonal cell, $A_{solid} = \frac{3\sqrt{3}}{2}a^2$, Equation 2 then gives the final expression for the relative density of the frustule:

$$\rho_{relative} = 1 - \frac{7\pi}{6\sqrt{3}}\left(\frac{d_c}{a}\right)^2 \frac{w_{cribrum}}{w_{total}} - \left(1 - \frac{1}{\sqrt{3}}\frac{t}{a}\right)^2 \frac{w_{areolae}}{w_{total}} - \frac{\pi}{6\sqrt{3}}\left(\frac{d_{b,inner}}{a}\right)^2 \frac{w_{basal}}{w_{total}} + \frac{\pi}{6\sqrt{3}}\left[\left(\frac{d_{b,outer}}{a}\right)^2 - \left(\frac{d_{b,inner}}{a}\right)^2\right] \frac{w_{rim}}{w_{total}} \qquad \text{Eq. (S7)}$$

Average measured values for d_c, $d_{b,inner}$, and $d_{b,outer}$ as well as measured values for $w_{cribrum}$, $w_{areolae}$, w_{basal}, w_{rim}, and w_{total} of each frustule beam is given in Table S1. Average values of t and a taken from 50 measurements of the indentation sample are 0.17 µm and 1.19 µm, respectively. For these values, the average relative density of each frustule beam is calculated and given in Table S1. The average relative density as determined by Eq. S7 is 36.4%.

Table S1. Pore dimensions and layer widths used in the general model for relative density.

	d_c (µm)	$d_{b,\,inner}$ (µm)	$d_{b,\,outer}$ (µm)	$w_{cribrum}$ (µm)	$w_{areolae}$ (µm)	w_{basal} (µm)	w_{rim} (µm)	$\rho_{relative}$
Sample 1	0.34	0.80	1.47	0.42	2.66	0.62	0.29	0.401
Sample 2	0.34	0.82	1.37	0.26	2.97	0.41	0.19	0.314
Sample 3	0.35	0.89	1.49	0.36	2.67	0.48	0.28	0.369
Sample 4	0.27	0.90	1.43	0.31	1.94	0.32	0.20	0.373
Sample 5	0.30	0.70	1.33	0.38	2.49	0.35	0.21	0.360

By taking advantage of the periodicity of the frustule we've been able to develop a general model, but the simplifying assumptions used could lead to a misrepresentation of the relative density of a beam sample. From SEM imaging it's seen that the pores in the cribrum layer are typically elliptic and vary in number per hexagonal cell and that foramen are not necessarily regularly spaced. Similarly, hexagonal areolae cells are irregular and the number of cell walls can vary from 5 to 6. In order to test the veracity of this general model, we used direct measurement of SEM images of each frustule beam to calculate $V_{cribrum}$, $V_{areolae}$, V_{basal}, and V_{rim}.

Ellipses were manually fit to each cribrum pore in the beam and the area of each ellipse was summed to provide the pore area, A_{pore}. The inverse area is determined by subtracting the pore area from the rectangular area, A_{beam}. Multiplying by the depth gives the cribrum volume $V_{cribrum}$.

$$V_{cribrum} = w_{cribrum}\left(A_{beam} - A_{pore}\right) \quad \text{Eq. (S8)}$$

A similar procedure was used to determine the volume of the basal layer, V_{basal}, by fitting circles to the inner diameter of each foramen.

$$V_{basal} = w_{basal}\left(A_{beam} - A_{foramina}\right) \quad \text{Eq. (S9)}$$

The difference in area between circles fit to the outer and inner diameter of each foramen provides the total projected area of the foramen rims, A_{rim}. Multiplying by the average thickness of the foramen rims gives the total rim volume, V_{rim}.

$$V_{rim} = w_{rim}(A_{beam} - A_{rim}) \quad \text{Eq. (S10)}$$

Determination of $V_{areolae}$ is difficult because the areolae walls are obscured by the cribrum and basal layers. To provide an estimation of the location of areolae walls, we generated a Voronoi diagram using the centers of the foramen as the seeds of each cell and bounded by the dimensions of the beam. This method generates a remarkably good match when applied to the visible areolae walls in the indentation plate shown in Figure 2e. $V_{areolae}$ could then be determined from the total length of the cell walls, $l_{areolae}$ multiplied by the average areolae wall thickness, *t* and depth of the areolae layer.

$$V_{areolae} = w_{areolae} * l_{areolae} * t \quad \text{Eq. (S11)}$$

The solid volume was determined using the average heights and depths of each beam:

$$V_{solid} = \frac{h_{cribrum}+h_{basal}}{2} * \frac{L_{cribrum}+L_{basal}}{2} * w_{total} \qquad \text{Eq. (S12)}$$

Where $L_{cribrum}$ and L_{basal} are the lengths of the cribrum and basal layers, respectively. These volumes were then directly substituted into Equation 1 to provide the measured relative density. The volumes $V_{cribrum}, V_{areolae}, V_{basal}, V_{rim}, V_{solid}$ and resulting relative densities are shown in Table S2. The average relative density as calculated from direct image measurements was 30.1%, showing decent similarity with the generalized model.

For analysis and discussion in the manuscript, we use the relative density calculated from image measurements as it provides a direct value for each unique beam sample.

Table S2. Layer and solid volumes for each beam sample and associated relative density.

	$V_{cribrum}$ (μm^3)	$V_{areolae}$ (μm^3)	V_{basal} (μm^3)	V_{rim} (μm^3)	V_{solid} (μm^3)	$\rho_{relative}$
Sample 1	25.05	20.38	44.80	4.20	280.65	0.336
Sample 2	17.98	28.46	35.84	1.38	322.33	0.260
Sample 3	38.40	39.75	57.39	5.01	455.15	0.309
Sample 4	20.52	16.30	21.80	1.80	196.42	0.308
Sample 5	27.84	22.17	28.83	2.51	277.52	0.293

2. Notch geometries for fracture samples

Variations in notch geometries were observed due to limited FIB resolution. Actual notch geometries for each fracture sample (Width X Height) were measured in the SEM and recorded in Table S3 (for POSS samples) and S4 (natural diatom samples). Since the variations are relatively small (variations within 10% in width and 5% in height), their effect on the sample stiffness are considered to be relatively minor, and the same equation for K_{1C} (Eq. S13) is used for all samples, while substituting different values to account for notch variations.

Table S3. Notch width and height measurements for POSS fracture samples.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
Height (nm)	518	510	557	520	510	524	528
Width (nm)	56	50	55	52	44	48	50
	Sample 8	Sample 9	Sample 10	Sample 11	Sample 12	Sample Average	
Height (nm)	488	515	540	485	496	515.9 ± 20.6	
Width (nm)	50	57	45	46	57	50.8 ± 4.6	

Table S4. Notch width and height measurements for natural diatom fracture samples.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample Average
Height (nm)	530	459	487	507	495.8 ± 30.1
Width (nm)	53	46	44	47	47.5 ± 3.9

Fracture toughness K_{1C}, for all samples was calculated as:

$$K_{1C} = \left[\frac{PS}{BW^{\frac{3}{2}}}\right] f\left(\frac{a}{w}\right) \qquad \text{Eq. (S13)}$$

where S, W and B are the dimensions of the sample, the initial crack length *a* is taken as the length of the notch, and $f(\frac{a}{w})$ is an empirically derived formula:

$$f\left(\frac{a}{w}\right) = \frac{3(\frac{a}{w})^{\frac{1}{2}}\left[1.99-\left(\frac{a}{w}\right)\left(1-\frac{a}{w}\right)\left(2.15-3.93\left(\frac{a}{w}\right)+2.7\left(\frac{a}{w}\right)^{2}\right)\right]}{2(1+2\frac{a}{w})(1-\frac{a}{w})^{\frac{3}{2}}} \quad \text{Eq. (S14)}$$

1. Aitken, Z. H., Luo, S., Reynolds, S. N., Thaulow, C. & Greer, J. R. Microstructure provides insights into evolutionary design and resilience of Coscinodiscus sp. frustule. *Proc. Natl. Acad. Sci.* **113,** 2017–2022 (2016).