Electronic Supporting Information:

A Self-Propagating System for Ge Incorporation into Nanostructured Silica

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1 Experimental details

1.1 Culture Conditions

Cells of the diatom *Thalassiosira pseudonana* (Hustedt) Hasle et Heimdal clone CCMP1335 were grown in 300 mL of an artificial seawater medium according to the North East Pacific Culture Collection protocol (http://www3.botany.ubc.ca/cccm/NEPCC/esaw.html), under constant stirring and illumination at 150 umol m^{-2} s^{-1}. Ge(IV) was added to cultures as $Ge(OH)_4$. Cultures were established with a fixed amount of silicic acid (100 µmol L^{-1}) and varying amounts of germanic acid (0 – 5.2 µmol L^{-1}) to generate ratios of $Ge(OH)_4$: $Si(OH)_4$ of 0, 1:200, 1:100, 1:60, 1:40, and 1:20. Cultures were inoculated at approximately 3 x 10^5 cells mL^{-1} and allowed to grow 2 days.

1.2 Preparation of cleaned diatom silica after $Ge(OH)_4$ treatment

Cells were harvested by centrifugation (10,000 x g for 10 min), and then resuspended in 10 ml of 1 mM diethyelentriaminepenataacetic acid (DTPA) made in seawater and incubated 10 min to remove surface-associated metals[1]. Samples were pelleted and washed once in water, and cell pellets were frozen at – 80° C until further processing. Organic material was removed by first dispersing the cell pellet in 250 µL water, then adding 3 mL concentrated sulfuric acid, and placing tubes into a boiling water bath for 10 min. Tubes were removed, allowed to cool, then a small amount (c.a. 40 mg) of solid KNO_3 was added and gently mixed, and tubes placed back in the boiling water bath for 10 min. Tubes were then removed, allowed to cool, an equal volume of water added, and then the tubes were centrifuged at 10,000 x g for 10 min. If the pellet was pigmented, it was resuspended again in water and treated as above. Usually the pellet was colorless after two treatments; if not the acid treatment was repeated. The pellet was then washed twice with water, and resuspended in 1 mL water.

1.3 Preparation of samples for ICP-OES analysis

Six hundred fifty microliters of cleaned cell wall material was pelleted, and dried under vacuum to remove traces of water, then 300 µL HF (Sigma Chemical Co. St. Louis MO, USA) was added to dissolve silica cell wall components. Tubes were incubated 45-60 min on ice, and then dried by vacuum under centrifugation for 6-11 h. Residual material was resuspended in 1 mL of 1% HNO_3 and incubated at 37° C for 30 min. The tubes were centrifuged at 20,000 x g for 5 min, the supernatant was removed and saved, and an

additional 1 mL of 1% HNO_3 was added to the tube and incubated at 37^o C for 30 min. This was repeated once more, and the combined 3 ml of supernatants were used for ICP-OES analysis. Ge standards for ICP-OES analysis were from SpexCertiprep (Metuchen NJ, USA). ICP-OES was done on a Hewlett Packard 3000 model DV used in the axial mode, at the Scripps Institution of Oceanography Unified Laboratory Facility.

1.4 Silica determination

An aliquot of cleaned cell wall material was resuspended in 4 ml of 0.5 M NaOH, and placed in a boiling water bath for 15 min to dissolve the silica. After cooling, 2 ml of 1N HCl was added to neutralize, and an aliquot removed for silicic acid measurement using the molybdate method of Strickland and Parsons [ii], but scaled down as follows. An aliquot of sample (estimated to result in a concentration of 20-40 μmol L^{-1}) was brought up to 1.5 mL with Milli-Q water. Then 0.6 mL of molybdate reagent was added, the tube vortexed, incubated 10 min, and then 0.9 mL reducing agent was added and the tube vortexed. Samples were incubated 3 h with occasional vortexing prior to determining the absorbance at 810 nm. Appropriate blanks were done to account for silicic acid in reagents, although this was negligible. Standards were dilutions of sodium hexafluorosilicate (Sigma Chemical Co. St. Louis MO, USA) in water. All determinations were in triplicate.

1.5 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was performed on *T. pseudonana* cell wall material that had been isolated and cleaned after $Ge(OH)_4$ treatment. Material was filtered onto a Whatman Cyclopore 1 μm PC10 membrane which was dried, sputter coated (Au/Pd), and then observed in an FEI Quanta 600 SEM at the Scripps Institution of Oceanography Unified Laboratory Facility.

i) J. G. Lee, S. B. Roberts and F. M. M. Morel, *Limnology and Oceanography*, 1995, **40** (6), 1056.
ii) J. D. H. Strickland and T. R. Parsons, *Bull. Fish. Res. Board. Canada*, 1968, **167**