AFOSR Project Report

Project Title: Complex-Shaped Microcomponents by the Reactive Conversion of Biological Templates

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Program Manager: Dr. Hugh C. De Long

Program Manager:
Biomimetics, Biomaterials, and Biointerfaceal Sciences
Air Force Office of Scientific Research
801 N. Randolph St., Room 732
Arlington, VA 22203-1977
E-mail: hugh.delong@afosr.af.mil
Phone: (703) 696-7722
Fax: (703) 696-8449

Principal Investigator: Prof. Ken H. Sandhage

School of Materials Science & Engineering
Georgia Institute of Technology
771 Ferst Drive
Atlanta, GA 30332-0245
E-mail: ken.sandhage@mse.gatech.edu
Phone: (404) 894-6882
Fax: (404) 894-9140

Co-Investigators: Dr. Rajesh Naik, Group Leader

Biotechnology Group, MLPJ Hardened Materials Branch
Air Force Research Laboratory, Wright-Patterson AFB
3005 P Street
WPAFB, OH 45433-7702
E-mail: rajesh.naik@wpafb.af.mil
Phone: (937) 255-3808 ext. 3180
Fax: (937) 255-1128

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Complex-Shaped Microcomponents by the Reactive Conversion of Biological Templates

Sandhage, Kenneth H.

Georgia Tech. Research Corporation
Georgia Institute of Technology
505 Tenth Street, NW
Atlanta, GA 30332-0420

Air Force Office of Scientific Research
4015 Wilson Blvd Room 713
Arlington, VA 22203-1954
Program Manager: Dr. Hugh De Long
(703) 696-7722, hugh.delong@afosr.af.mil

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This project has been aimed at: 1) developing a better understanding of the manner in which the morphology and nanostructure of biologically-derived silica microtemplates evolve during the course of reactive conversion, and 2) determining which reaction parameters have the greatest impact on changes in morphology during such reactive conversion. The most significant accomplishments have been:

- Demonstration (via high resolution TEM analyses) that the reaction of SiO$_2$ diatom frustules with Mg(g) at 650°C results in direct conversion into nanocrystalline MgO and Si (≤15 nm) without the formation of intermediate silicate phases.

- Syntheses of MgO-converted frustules with minimal secondary phases (Si or Mg$_2$Si) by development of an optimized thermal treatment and selective dissolution treatment.

- Identification and control of critical processing parameters to avoid active vaporization and gas-phase-assisted coarsening during the metathetic conversion of SiO$_2$ frustules into TiO$_2$.

- Successful syntheses of ZrO$_2$ frustule replicas via a new two-step reaction process (conversion of SiO$_2$ into MgO via Mg(g) reaction; then conversion of MgO into ZrO$_2$ via ZrCl$_4$(g) metathetic reaction and selective MgCl$_2$ dissolution in water).
Objectives: 1) To develop a better understanding of the manner in which the morphology and nanostructure of biologically-derived silica microtemplates evolve during the course of reactive conversion, and 2) to determine which reaction parameters have the greatest impact on changes in morphology during such reactive conversion.

Summary of Effort: Work over the past year has focused on the conversion of silica-based diatom frustules by the net reactions:

1) $2\text{Mg}(g) + \text{SiO}_2(s) \Rightarrow 2\text{MgO}(s) + \{\text{Si}\}$  
2) $\text{TiF}_4(g) + \text{SiO}_2(s) \Rightarrow \text{TiO}_2(s) + \text{SiF}_4(g)$  
3) $\text{ZrCl}_4(g) + 2\text{MgO}(s) \Rightarrow \text{ZrO}_2(s) + 2\text{MgCl}_2(l)$

where $\{\text{Si}\}$ refers to Si in a Mg-Si liquid. Conversion of SiO$_2$-based diatom frustules into MgO, TiO$_2$, and ZrO$_2$ has been achieved with a preservation of the starting biogenic shapes.

Complete conversion of diatom frustules into MgO via net reaction (1) has been achieved at temperatures as low as 650°C within 2 h. Under these conditions, polycrystalline MgO frustules were generated with crystallite sizes of only 10-15 nm (i.e., much finer than that for conversion at 900°C). TEM analyses of partially-converted specimens revealed the presence of MgO and Si nanocrystals (<5 nm in dia.) in close proximity within an unreacted silica matrix; that is, the conversion of SiO$_2$ appears to proceed directly without the formation of intermediate silicate phases (as has been reported in the literature for the reaction of Mg(g) gas with bulk SiO$_2$ at 1150°C). The solid Si product then reacted with excess Mg(g) to form Mg$_2$Si. The amount of Mg$_2$Si generated by this latter reaction was minimized by controlling the Mg:SiO$_2$ reactant ratio and the reaction temperature and time. A sodium hydroxide solution was then used to selectively dissolve away the Si product of reaction (1) to yield MgO-based frustule replicas.

Complete conversion of SiO$_2$-based diatom frustules into TiO$_2$ via the net reaction (2) has been accomplished at only 350°C via a two-step process: i) the formation of TiOF$_2(s)$ via reaction with TiF$_4(g)$ and then ii) conversion of TiOF$_2(s)$ into TiO$_2(s)$ via reaction with O$_2(g)$. By controlling the TiF$_4$:SiO$_2$ reactant ratio, the heating rate, and the peak reaction temperature and time during the first stage of reaction, active vaporization (due to TiOF$_2(s)$ formation away from the frustule surface) and coarsening (via a gas phase diffusion mechanism) were minimized so as to yield TiOF$_2$ replicas that preserved the starting frustule shape and fine features.

A two-step reaction process has also been developed to allow for chemical conversion of the silica-based diatom frustules into zirconia. Initial attempts to form ZrO$_2$ replicas via direct reaction of ZrF$_4(g)$ with SiO$_2(s)$ resulted in disintegration of the frustules. To avoid the formation of volatile Si-O-bearing products associated with such disintegration, the SiO$_2$ frustules were first converted into MgO via net reaction (1). The MgO replicas were then exposed to ZrCl$_4(g)$ at 650°C for 2 h to allow for reaction (3). The latter reaction yielded tetragonal ZrO$_2$ replicas along with a liquid MgCl$_2$ product that then solidified during cooling. Selective dissolution of the solidified magnesium chloride in water then yielded free-standing zirconia frustule replicas.

The reaction-based processes developed in this BioInspired Concepts (BIC) project have enabled the syntheses of frustule-shaped structures that exhibit:

i) luminescence (from Eu/BaTiO$_3$ coatings applied to compatible MgO-converted frustules)
ii) gas sensing (due to rapid changes in the conductivity of TiO$_2$ frustules resulting from small changes in ethanol vapor pressure)
iii) organophosphor destruction (pesticide-bearing solutions have exhibited rapid reaction with TiO$_2$-converted frustules)
Accomplishments/New Findings:

- Demonstration (via high resolution TEM analyses) that the reaction of SiO$_2$ diatom frustules with Mg(g) at 650°C results in direct conversion into nanocrystalline MgO and Si ($\leq$15 nm) without the formation of intermediate silicate phases.
- Syntheses of MgO-converted frustules with minimal secondary phases (Si or Mg$_2$Si) by development of an optimized thermal treatment and selective dissolution treatment.
- Identification and control of critical processing parameters to avoid active vaporization and gas-phase-assisted coarsening during the metathetic conversion of SiO$_2$ frustules into TiO$_2$.
- Successful syntheses of ZrO$_2$ frustule replicas via a new two-step reaction process (conversion of SiO$_2$ into MgO via Mg(g) reaction; then conversion of MgO into ZrO$_2$ via ZrCl$_4$(g) metathetic reaction and selective MgCl$_2$ dissolution in water).

These new accomplishments have made possible the development (in a MURI project) of luminescent diatom frustules (for microtagging applications), single diatom frustule gas sensors (for minimally-invasive sensing), and diatom frustules that rapidly destroy organophosphorous compounds (potentially for removing chemical warfare agents).

Reactive Conversion into MgO Frustules

*Phase and Nanostructural Evolution at 650°C*

In order to slow down the rate of reaction (to enable evaluation of the earliest stage(s) of the MgO conversion process) *Aulacoseira* diatom frustules were exposed to Mg(g) at only 650-700°C. The frustules were placed inside and near one end of a mild steel tube. Mg granules (99.8% purity, 0.3-1.7 mm size) were placed at the other end of the tube. An excess of Mg granules relative to silica frustules (Mg:SiO$_2$ molar ratio = 9.9:1) was placed inside the steel tubes in order to ensure that the source of magnesium vapor was not depleted during the course of the reaction. The tube was then crimped and welded shut within an Ar atmosphere inside a glove box. The resulting sealed steel ampoule was then bent into an inverted “V” shape, in order to ensure that the silica frustules remained physically separated from the magnesium powder. The sealed steel ampoules were then heated at 5-7°C/min to 650°C or 700°C and held for 0.5-2 h.

A secondary electron image of a starting *Aulacoseira* diatom frustule, and an associated energy-dispersive x-ray (EDX) pattern are shown in Figures 1a and 1b, respectively (note: the gold peak was obtained from a thin coating applied to avoid electron beam charging).

Fig. 1. a) Secondary electron image and b) EDX analysis of an *Aulacoseira* diatom frustule.
Upon heating to 650-700°C, the silica frustules within the sealed steel tube were exposed to magnesium gas generated by evaporation from the magnesium granules. Magnesium gas may undergo the following oxidation-reduction (displacement) reaction with silica:

\[ 2\text{Mg}(g) + \text{SiO}_2(s) \rightarrow 2\text{MgO}(s) + \text{Si}(s) \]  (4)

A secondary electron image of an *Aulacoseira* frustule that had been exposed to Mg(g) for 0.5 h at 700°C is shown in Fig. 2a. The cylindrical shape, narrow channels, and rows of fine pores were well preserved in this reacted frustule. A TEM image of a cross-section of such a reacted frustule is shown in Fig. 2b. The cross-section was comprised largely of crystallites with diameters ≤50 nm, although a few larger crystallites (100-150 nm diameter) were also detected. EDX (Fig. 2c) and electron diffraction (Fig. 2d) analyses revealed that the reacted frustule was comprised of magnesium oxide (periclase), with very little silicon detected throughout the cross-section (the gold peak in Fig. 2c was obtained from a coating applied to the specimen for SEM analysis prior to ion milling; the copper peak was obtained from the grid used to support the specimen cross-section in the TEM). The loss of silicon was a result of the formation of a Mg-Si
liquid (a eutectic liquid can form at 638°C in the Mg-Si system) that poured out of the frustule. The solidified Mg-Si liquid can be seen below the MgO-converted frustule in Fig. 2a. The data in Fig. 2 indicate that *Aulacoseira* frustules can be fully converted into a nanocrystalline MgO-based replica within only 0.5 h of exposure to Mg(g) at 700°C.

In order to evaluate the phase and nanostructural evolution during such shape-preserving reactive conversion, the reaction temperature was further reduced to 650°C to slow the rate of reaction. XRD analyses of the *Aulacoseira* diatom frustules before and after exposure to Mg(g) for various times at 650°C are shown in Fig. 3. For exposure times of 1 h or less, only diffraction peaks for SiO₂ (as cristobalite) were detected. However, from 1.5 to 2 h of exposure to Mg(g), MgO, Si and Mg₂Si formed at the expense of cristobalite. Indeed, after the 2 h treatment, the diffraction peaks for cristobalite vanished. Bright field TEM images, and associated electron diffraction patterns, of ion-milled cross-sections obtained from specimens exposed to Mg(g) for 1-2 h at 650°C are shown in Figs. 4a-f. Consistent with XRD analyses, selected area electron diffraction (SAED) analyses of the cross-section of the 1 h specimen in Fig. 4a revealed only diffraction associated with cristobalite (hkl values associated with

![XRD Analysis](image)

Fig. 3. XRD analyses of *Aulacoseira* diatom frustules a) before and b)-e) after exposure to magnesium gas at 650°C for 0.5, 1, 1.5 and 2 h.

several of these diffraction spots are indicated). Prolonged exposure of this specimen cross-section to the electron beam in the TEM also resulted in amorphization, as has been observed by other authors during TEM analyses of silica-based specimens. After 1.5 h of reaction, the specimen cross-section was found to be partially reacted (Fig. 4b). SAED analysis of the reaction zone (Fig. 4e) revealed the presence of MgO and Si, consistent with reaction (1). The absence of electron or x-ray diffraction peaks (Figs. 3d and 4e) for magnesium silicates (e.g., forsterite, Mg₂SiO₄; enstatite, MgSiO₃) suggested that these compounds were not involved as intermediate products in reaction (1). Consistent with such diffraction analyses, a high-resolution TEM image (Fig. 5) of this cross-section obtained at the location of the interface between the reacted zone and the unreacted silica revealed the presence of only MgO and Si nanocrystals (< 5 nm in diameter) in an amorphous matrix. The structure generated after 2 h of exposure to Mg(g) at 650°C is shown in Fig. 4c. The nanocrystalline reaction zone completely penetrated this specimen. SAED analysis revealed a mixture of MgO, Si, and Mg₂Si in the
reaction zone. The latter compound was generated by the continued reaction of the silicon product from reaction (1) with magnesium gas, as shown below.

\[ 2\text{Mg(g)} + \text{Si(s)} \Rightarrow \text{Mg}_2\text{Si(s)} \] (5)

As discussed above, further reaction of this \( \text{Mg}_2\text{Si} \) product with \( \text{Mg(g)} \) leads to the formation of a \( \text{Mg-Si} \) liquid that tends to pour out of the converted frustule onto the underlying steel substrate (Fig. 2a), so as to leave a nanocrystalline \( \text{MgO} \)-based structure. The width of the most intense x-ray diffraction peak for magnesia (the (200) peak near \( \theta = 43 \) degrees) was obtained from several batches of specimens exposed to the \( 650^\circ\text{C}/2 \) h heat treatment. Insertion of this data into the Scherrer equation yielded average magnesia crystallite sizes of 12-15 nm. These XRD-derived values were consistent with the fine nanocrystallites observed in the TEM images of Figs. 4b and c. These \( \text{MgO} \) grains were also considerably finer, by several orders of magnitude, than those generated upon exposure of diatom silica to magnesium gas at \( 900^\circ\text{C} \) for 4 h.

Prior work by other authors on the reaction of sintered \( \text{SiO}_2(s) \) tablets or quartz crystals with \( \text{Mg(g)} \) at much higher temperatures (e.g., \( 1150^\circ\text{C} \)) have indicated that \( \text{Mg}_2\text{SiO}_4(s) \) and \( \text{SiO(g)} \)

formed as intermediate reaction products via the following reaction steps:

\[ 3\text{SiO}_2(s) + 2\text{Mg(g)} \Rightarrow \text{Mg}_2\text{SiO}_4(s) + 2\text{SiO(g)} \] (6)
\[ \text{Mg}_2\text{SiO}_4(s) + 2\text{Mg(g)} \Rightarrow 4\text{MgO(s)} + \text{Si(s)} \] (7)
\[ 2\text{SiO(g)} + 2\text{Mg(g)} \Rightarrow 2\text{MgO(s)} + 2\text{Si(s)} \] (8)

Fig. 4. a)-c) TEM images of cross-sections of *Aulacoseira* frustules exposed to \( \text{Mg} \) gas at \( 650^\circ\text{C} \) for 1, 1.5, and 2 h respectively. d)-f) SAED patterns obtained from a)-c) respectively.
While the formation of Mg$_2$SiO$_4$(s) and SiO(g) via reaction (6) was thermodynamically favored at 1150°C, this reaction was not favored at 650°C in the present work. The thermodynamic ratio of the Mg(g) to SiO(g) partial pressures that is required for reaction (6) to proceed spontaneously to the right at 650°C is 48, compared to only 6.5X10^{-2} at 1150°C. The amount of Mg relative to SiO$_2$ that was sealed in the steel ampoules in the present work (a molar Mg:SiO$_2$ ratio of 9.9:1) was insufficient to allow for the occurrence of this intermediate reaction.

The basic understanding of the phase and nanostructural evolution obtained from the work discussed above has enabled the development of optimized processing treatments over the past year for the conversion of SiO$_2$ frustules into MgO-based frustules containing minimal secondary phases (i.e., Si or Mg$_2$Si). By minimizing these secondary phases, the MgO frustules could be utilized as chemically-compatible substrates for other functional ceramic coatings (e.g., luminescent Eu-doped BaTiO$_3$) and as structures for microfluidic mixing devices (e.g., based on electroosmotic flow). Optimization of the MgO conversion conditions is discussed below.

**Optimized Processing of MgO-converted Frustules**

Several processing changes have been introduced in order to reduce the relative amounts of undesired second phases (e.g., Si, Mg$_2$Si) in the MgO-converted frustules. A schematic of a typical reaction configuration within the sealed iron tubes is shown in Fig. 6a. At the start of the experiments, the diatom frustules and solid magnesium reactants were placed at opposite ends of the iron tube. The tube was then crimped in the middle (to avoid physical mixing of the reactants) and the ends were welded shut. Upon heating the magnesium vaporized and diffused to the frustules, whereupon the displacement reaction commenced. As shown in Figs. 6a and 6b, distinct reaction zones were detected within partially-converted frustule powder beds. The distinct interfaces and colors of these zones enabled separation and analyses (XRD, SEM, EDX) of the phases within each zone. The region located nearest the magnesium gas source was observed to possess a grey or blue-grey color, which was a result of the presence of Mg$_2$Si. A secondary electron image of this phase is shown in Fig. 6c. The darker intermediate zone was comprised of a mixture of MgO and Si. A secondary electron image of a frustule from within this zone, exhibiting Si nodules, is shown in Fig. 6d. The brown zone at the opposite end of the
powder bed contained residual unreacted silica. The distribution of these products was consistent with the reaction steps identified above; that is, \( \text{SiO}_2 \) is first converted into a mixture of \( \text{MgO} \) and \( \text{Si} \), and the \( \text{Si} \) then reacts with excess \( \text{Mg}(g) \) to form \( \text{Mg}_2\text{Si} \).

The \( \text{Mg}:\text{SiO}_2 \) reactant ratio, the reaction temperature, and the reaction time were varied to allow for complete conversion of the \( \text{SiO}_2 \) into \( \text{MgO} \) while minimizing the amount of \( \text{Mg}_2\text{Si} \) produced. With a \( \text{Mg}:\text{SiO}_2 \) ratio of 2:1 and a reaction temperature/time of 900°C/1.5 h, the frustule powder bed was converted into a mixture of \( \text{MgO} \) and \( \text{Si} \) with minimal \( \text{Mg}_2\text{Si} \), as shown in Fig. 7a. The residual silicon was then selectively dissolved away with an aqueous sodium hydroxide solution. The NaOH in this solution was adjusted to achieve a NaOH:Si molar ratio of 2:1 to allow for the formation of soluble sodium metasilicate (\( \text{Na}_2\text{SiO}_3 \)). The Si-depleted frustules were then rinsed with boiling DI water. XRD analysis and secondary electron images of the resulting MgO frustules are shown in Figs. 7b and 8, respectively. It is important to note that the development of processing methods for removing \( \text{Mg}_2\text{Si} \) (through adjustment of reaction conditions) and \( \text{Si} \) (through selective dissolution) were essential for the use of MgO frustules as: i) substrates for conformal luminescent coatings (i.e., Eu-doped \( \text{BaTiO}_3 \) coatings on MgO), and ii) 3-D micro-structures for incorporation in electro-osmotic mixing devices (i.e., to avoid bubble formation due to the reaction of residual \( \text{Mg}_2\text{Si} \) with water).

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Fig. 6. a) Schematic illustration of the sealed iron reaction tube showing the positioning of reactants and the typical progression of products through the frustule powder bed. b) Optical image of a frustule powder bed after reaction for 3 h at 850°C. Secondary electron images revealing the \( \text{Mg}_2\text{Si} \) and \( \text{Si} \) secondary phases are shown in c) and d), respectively.
Reactive Conversion into TiO$_2$ (anatase) Frustules

A two-step reaction process has been used to convert silica-based diatom frustules into titania replicas. The first step involves the following metathetic reaction of SiO$_2$ with TiF$_4$(g) to yield the oxyfluoride, TiOF$_2$:

$$2\text{TiF}_4(g) + \text{SiO}_2(s) \Rightarrow 2\text{TiOF}_2(s) + \text{SiF}_4(g)$$ (9)

In the second step, the TiOF$_2$ is converted to TiO$_2$ by reaction with O$_2$(g):

$$\text{TiOF}_2(s) + \text{O}_2(g) \Rightarrow \text{TiO}_2(s) + \text{F}_2(g)$$ (10)

In this work, solid TiF$_4$ was utilized as a low-temperature source of TiF$_4$ vapor (note: the sublimation temperature of TiF$_4$(s) is 285°C). 100 milligrams of Aulacoseira diatom frustules were placed within a titanium tube along with solid TiF$_4$. As discussed above for the Mg/SiO$_2$ reactions, both ends of the tube were then crimped and welded shut. The specimen-bearing tube was then heated to the desired reaction temperature. At the end of this treatment, the tube was pushed out of the hot zone of the horizontal tube furnace. For the second reaction, the specimens were heated to 350°C for 2 h in pure, flowing oxygen.

Several processing parameters associated with the first reaction step have been found to be particularly critical with regards to shape preservation:

i) the TiF$_4$:SiO$_2$ reactant ratio
ii) the peak reaction temperature and time
iii) the heating rate

Initial experiments conducted at 500-700°C for 2 h using TiF$_4$:SiO$_2$ molar ratios of $\geq$4.9:1 within the sealed Ti tubes resulted in disintegration of the starting SiO$_2$ frustules and the formation of relatively coarse plate-shaped TiO$_2$ crystals (5-10 μm X 5-10 μm X 0.5-1 μm thick). Such active vaporization of the silica frustules was avoided by lowering the reaction temperature to 350°C and reducing the TiF$_4$:SiO$_2$ molar ratio to 2.4:1 within the Ti tubes. After 2 h under these conditions, the overall shape and fine features of the reacted frustule were quite similar to those
of the starting frustules, as shown in Fig. 8a below. EDX and XRD analyses confirmed that the frustules had been converted completely into TiOF$_2$. Further reduction in the TiF$_4$:SiO$_2$ molar ratio to 1.6 resulted in negligible reaction of the frustules within 2 h at 350°C.

An increase in the reaction temperature from 350°C to 450°C for a fixed time (2 h), a fixed heating rate (5°C/min), and a fixed TiF$_4$:SiO$_2$ ratio resulted in appreciable coarsening of the TiOF$_2$ grains, as shown in Figs. 8a and 8b. For a constant peak temperature/time of 350°C/2 h, a reduction in the heating rate also yielded an increase in TiOF$_2$ crystallite size (Figs. 8c and 8d). At such modest temperatures and times, it is not likely that such coarsening occurred by a solid-state diffusion mechanism. Given that a gaseous TiOF$_2$ species can exist at these temperatures, it is likely that such rapid coarsening occurred via transport through the gas phase; that is, by the evaporation of small TiOF$_2$ particles and condensation onto larger TiOF$_2$ particles (Ostwald ripening) as illustrated in Fig. 8e. Such gas-phase-assisted coarsening has been observed in a number of ceramic systems with volatile species (notably by D. W. Read: “Vapor Transport and Microstructure Development in Ceramics,” Journal of Metals, 36 (12) 18-18, 1984).

By controlling the heating rate, peak reaction temperature and time, and TiF$_4$:SiO$_2$ molar ratio, the active vaporization of silica and the rapid vapor-phase-assisted coarsening of TiOF$_2$ could be minimized so as to yield TiOF$_2$ and then TiO$_2$ replicas that retained the shapes and fine features of the starting diatom frustules.

**Fig. 8.** Secondary electron images of TiOF$_2$-converted frustules generated by reaction for 2 h at: a) 350°C (heating rate = 5°C/min), b) 450°C (heating rate = 5°C/min). Higher magnification images of TiOF$_2$-converted frustules after reaction for 2 h at 350°C with heating: c) at a rate of 5°C/min and d) via thrusting into pre-heated furnace.
Fig. 8 (cont.). A schematic illustrating gas-phase-assisted coarsening is shown in e).

**Reactive Conversion into ZrO₂ Frustules**

The direct reaction of ZrF₄(g) with SiO₂ diatom frustules was conducted within sealed nickel alloy tubes for 2 h over a range of temperatures (250-800°C) and ZrF₄:SiO₂ molar ratios (0.36 to 3.6). For reaction temperatures at or below 350°C, no reaction was detected within 2 h. At higher temperatures and for all ZrF₄:SiO₂ ratios examined, the silica frustules were observed to disintegrate, as shown in Fig. 9.

Fig. 9. Secondary electron image of a disintegrating *Aulacoseira* frustule after exposure to ZrF₄ gas at 600°C for 2 h.

An entirely different two-step reaction process was then adopted so as to avoid such active vaporization. In the first step, the silica frustules were converted into MgO, as per the oxidation-reduction conditions discussed above. The magnesia was then exposed to ZrCl₄(g) to allow for the following net reaction:

\[
\text{ZrCl}_4(g) + \text{MgO}(s) \rightarrow \text{ZrO}_2(s) + \text{MgCl}_2(l) \quad (11)
\]
The magnesium chloride product, which solidified upon cooling to room temperature, was then be removed by selective dissolution in water. To test this new approach, the magnesia-converted frustules were sealed along with zirconium chloride (ZrCl₄:MgO molar ratio = 5.8) in nickel alloy tubes. The tubes were then heated at 5°C/min to a peak temperature of 325-650°C for 2 h. The reacted specimens were then immersed and stirred in water heated to 80°C for 1 h. For reaction temperatures at or below 475°C, significant amounts of residual unreacted magnesium oxide were detected. However, reaction for 2 h at 650°C resulted in complete conversion of the magnesia into tetragonal zirconia and magnesium chloride. An XRD pattern of such reacted specimens (after dissolution of the magnesium chloride in water) is shown in Fig. 10. Secondary electron images of zirconia-converted frustules and a corresponding EDX pattern are shown in Figs. 11a-c. The zirconia replica retained the cylindrical shape of the starting Aulacoseira frustule.

Fig. 10. XRD pattern obtained from a ZrO₂-converted frustule generated by exposure of a MgO-converted frustule to ZrCl₄(g) for 2 h at 650°C followed by immersion in stirred water at 80°C for 1 h.
Fig. 11. a), b) Secondary electron images, and c) an associated EDX pattern obtained from a ZrO$_2$-converted frustule generated by exposure of a MgO-converted frustule to ZrCl$_4$(g) for 2 h at 650°C followed by immersion in stirred water at 80°C for 1 h.
Personnel Supported:
Faculty: Prof. Ken H. Sandhage
Graduate Students: Mr. Samuel Shian, Mr. Shawn Allan, Mr. Matthew Dickerson

Publications:

*supported by an AFOSR MURI project.

Interactions/Transitions:
The Sandhage group has moved from Ohio State University to the Georgia Institute of Technology. New facilities that have been set up at Georgia Tech for the Sandhage group over the past year include:

- a diatom culturing facility (with the advice and help of M. Hildebrand, UCSD/Scripps)
- a biopanning facility (with the advice and help of R. Naik, AFRL)
- new thermal processing facilities (with the advice and help of R. Rapp, Ohio State)

A new state-of-the-art x-ray characterization facility (which includes a high-temperature x-ray diffraction system for the work in this BIC program) has also been established over the past year by R. Snyder, a collaborator with K. Sandhage.

The reaction-based processes developed in this BioInspired Concepts (BIC) project have enabled the syntheses of frustule-shaped structures (via a MURI project) that exhibit:

i) luminescence (from Eu/BaTiO$_3$ coatings applied to compatible MgO-converted frustules)
ii) gas sensing (due to rapid changes in the conductivity of TiO$_2$ frustules resulting from small changes in ethanol vapor pressure)
iii) organophosphor destruction (pesticide-bearing solutions have exhibited rapid reaction with TiO$_2$-converted frustules)
Luminescence measurements have been obtained via a new collaboration with Prof. Chris Summers of the MSE Dept. at Georgia Tech. Gas sensing measurements have been obtained via a new collaboration with Prof. Meilin Liu of the MSE Dept. at Georgia Tech. Organophosphor destruction kinetics have been measured in a new collaboration with Prof. Ching-Hua Huang of the Civil and Environmental Engineering Dept. at Georgia Tech.

Other interactions include the following technical presentations:


