

**Gas-solid displacement reactions for converting silica
diatom frustules into MgO and TiO₂**

by

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1 INTRODUCTION

Technology for the microfabrication of freely moving parts began with a Bell Labs microgear spun by an air jet, and electrostatic silicon micro motors in the mid-1980s. It continued with development work on micropositioning of optics, miniature heat exchangers, small fluidic devices, and chemical reaction chambers¹. Recently, there has been a great deal of interest centered on the design and manufacture of devices of nanometer proportions and this speculation has spawned a new industry named, nanotechnology. Despite the technological and economic promise of this technology, current commercial micro/mesofabrication methods have largely been based upon two-dimensional processing principles which is not well suited to the low-cost mass production of three-dimensional micro devices with complex geometries and meso/nanoscale features².

Diatoms are three dimensional (3D) microstructures from nature that provide a practical alternative for nanotechnology and microfabrication³. Diatoms (Figure 1) are single-celled micro algae that form rigid cell walls (frustules) composed of amorphous silica. Their dimensions can range from less than 1 micron to several hundreds of microns. They are distributed throughout the world in aquatic, semi-aquatic and moist habitats, and extremely abundant in freshwater and marine ecosystems. Diatoms are thought to be responsible for up to 25% of the world's net primary production of organic carbon (by transforming of carbon dioxide and water into sugars by photosynthesis). Approximately 10^5 unique diatom frustule shapes have been claimed to exist in nature. The frustules are composed of two valves that fit together like a petri-dish, connected to each other by one or more girdle bands. The frustule wall consists of a nanoporous assembly of silica nanoparticles. They absorb soluble silica from water even at extremely low concentrations and metabolize and deposit it as an external skeleton. Continued reproduction of a single parent diatom can yield large numbers of descendant diatoms, each of which possesses a frustule with the same microshape and meso/nano features². Each mitotic division results in the formation of two differently sized daughter cells, one that is the same size as the parent and one that is slightly smaller. Therefore, over successive generations the mean cell size of a population decreases and standard deviation about this mean increases. It is believed that

when a cell decreases in size to a diameter of less than about 30 to 40 % of the maximum diameter for a given species, sexual reproduction initiates. This enables an entirely new frustule to be generated that is many times larger than either parent. Importantly, these newly formed large cells rapidly resume asexual reproduction and are essentially “immune” to sexual reproduction until an appropriate small cell size is obtained⁴.

Their specific morphological features (a gigantic variety of silicified networks, pores, tubes and ribbons), create high surface area. For instance, *thalassiosira descipiens* has a specific surface area of $258 \text{ m}^2/\text{g}$ ⁵. The remnants of diatom blooms sink to the ocean floor where they end up as diatomaceous deposit and reappear to the surface after millions of years of aging as ‘diatomaceous earth’. Specific surface area of diatomaceous earth has been determined as $22 \text{ m}^2/\text{g}$ ⁶. Crystalline phases within the frustules have not been reported, but it was suspected that at domains $< 10 \text{ nm}$ (below the limit of XRD) crystalline phases exist⁷.

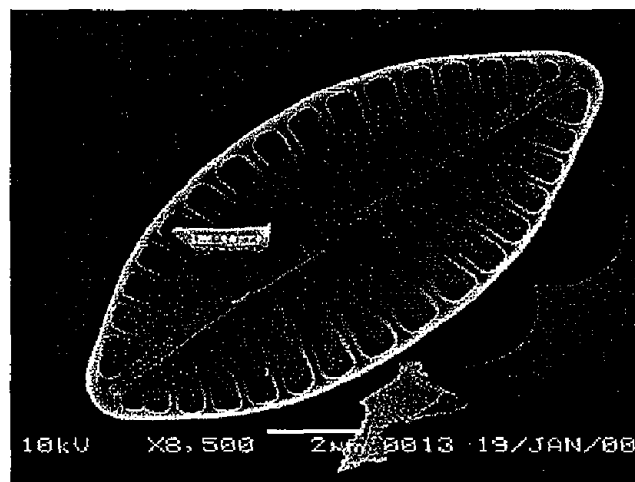


Figure 1: Scanning electron micrograph of a diatom frustule.
(<http://www.mta.ca/~jehrman/kouch.htm>)

The range of potential applications for diatom frustules is limited by the properties of silica. Biological, chemical, mechanical, thermal, and electrical properties of silicon-based compositions are not appropriate for all device applications. Diatoms could be used as biofactories to generate large numbers of 3D structures with reproducible micro-to-nanoscale features.

The fluid/solid displacement reactions can be used to convert macropreforms of oxides into new oxides or oxide bearing composites that retain the preform shape and dimensions. Silica-based diatom frustules can be converted into new compositions through the use of shape-preserving displacement reactions².

There are many criteria that have to be satisfied to obtain successful conversion reactions. First, the reaction that will be carried out should be favored thermodynamically. It is a fact that reactions which have slightly positive Gibbs free energy can also run under certain conditions, i.e. removing the products from the system, kinetically favored reactions. To be able to retain the shape of the frustule the volume of the product should be similar to the volume of the template. The reaction should kinetically lead to completion and compositional homogeneity and reproducibility should be attained. A reasonable temperature and time for the reaction would provide applicable setups for the experiments.

It is the primary objective of this research to explore the possibility of converting silica diatom frustules into other compositions using gas-solid displacement reactions while retaining the shape of the frustule.

2 LITERATURE REVIEW

2.1 Gas-Solid Reactions

The gas-solid reaction may proceed to yield the final states such as: physisorbed gas molecules on the surface, chemisorbed gas molecules on the surface, dissociation of the incident gas without modification of the surface, chemical interaction to yield a chemically modified solid surface such as a solid solution or a new solid phase, chemical interaction with the surface to yield liquid products, chemical interaction with the surface material to yield vapor-phase products⁸. The type of the reactions that are carried out in this work goes into the category that modifies solid surface as result of a chemical interaction.

2.1.1 Gas-Solid Reaction Steps

The overall process of most of the gas-solid reaction systems may involve several intermediate steps as following:

- 1) Diffusion (mass transfer) of reactants and products from the bulk of the gas phase to the surfaces of the reacting solid particle.
- 2) Diffusion of gaseous reactants or gaseous products through the solid reaction product or through the partially reacted solid.
- 3) Adsorption of the gaseous reactants on and desorption of reaction products from the solid surfaces.
- 4) The actual chemical reaction between the adsorbed gas and the solid⁹.

When a gas is brought into contact with a solid, due to the attractive forces between the surface and the adsorbed species, adsorption occurs on a solid surface. There are two types of adsorption; chemical adsorption (chemisorption), and physical adsorption (physisorption). In chemisorption the adsorbed species forms a chemical bond with the surface, and usually gas-solid reactions and catalysis on solid surfaces are due to the chemisorption. The heat evolved is higher than it is in physisorption. No more than a monolayer of adsorbed species can be formed, but it is specific to the particular gas and solid. Chemisorption is generally slow, since it requires a high activation energy, and

generally occurs at a significant rate in a higher temperature range. In physisorption, the adsorbed species are attracted to the surface by van der Waals or dispersion forces which are much weaker than the attraction forces in chemisorption. Physisorption can form many adsorbed layers, because of the long range nature of the forces involved. In general, physical adsorption requires no or a low activation energy, and occurs at temperatures below the boiling point of the adsorbate⁹.

2.2 Thermodynamics and Kinetics of Reactions

Thermodynamic feasibility of a reaction is very important as a first step in deciding whether a reaction is likely to occur within the realm of practical experimental conditions. The change in free energy is related to the reaction quotient of a reaction by the following equation:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

The chemical change that takes place in any reaction may be represented by a stoichiometric equation such as



The rate equation or rate expression of the reaction can be written as

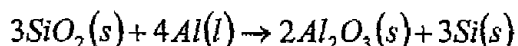
$$R = k[A]^m[B]^n$$

The proportionality constant, k , is called the rate constant. The exponent m is the order of the reaction with respect to reactant A, and n is the order of the reaction with respect to reactant B¹⁰.

2.3 Displacement Reactions

A single displacement reaction is characterized by an atom or an ion of a single compound replacing a different atom or ion. Double displacement reactions may also be called metathesis reactions. In this type of reaction, elements or ions from two compounds displace each other to form new compounds. Double displacement reactions may occur when one product is removed from the solution as a gas or precipitate or when two species combine to form a weak electrolyte that remains undissociated in solution.

Displacement solid-liquid reactions with molten metals were used to convert shaped macropreforms into new compositions that retain the starting preform shape. In 1995, Breslin *et al.* reported that they generated near net-shape Al_2O_3 and Al composites by immersing dense preforms of amorphous SiO_2 into molten Al at 1000-1300 °C with the reaction¹¹:



In this reaction the product Si dissolves back into bath and the resulting microstructure consist of a continuous network of alumina interpenetrated by a continuous network of Al. Near net-shaped $\text{Al}_2\text{O}_3/\text{Al}$ -Si composites were generated by Loehman *et al.* by exposing dense preforms of polycrystalline mullite to molten Al or Al-Si. Claussen *et al.* rapidly infiltrated porous oxide preforms with molten Al by gas pressure infiltration or squeeze casting^{12,13}. Dense and homogeneous Al_2O_3 and TiAl_3 networks have been fabricated with the reaction of Al with TiO_2 in $\text{TiO}_2/\text{Al}_2\text{O}_3$ preform. Schutte *et al.* reported a fast chemical reaction of a metal with a non-metallic compound, in which a metal silicide is generated that retains the original shape of the metal. They performed the reactions of iron, nickel, and chromium with gaseous silicon chloride and obtained the silicides of these metals with retention of morphology¹⁴. Sandhage *et al.* obtained dense ceramic/metal composites by converting porous ceramic-bearing preforms by using reactive melt infiltration¹⁵. They reported the first use of gas/silica displacement reactions to convert biologically derived silica meso/nanostructures (such as diatom frustules) into new compositions, with retention of shape and fine features². They demonstrated the process by converting diatom frustules into MgO nanostructures. Prior to work of Sandhage *et al.*, the shape preserving displacement reactions were limited to macroscopic shapes and the level of control of the morphology was generally limited to multi-micron scale. Recent work demonstrated that the displacement reactions may be employed for articles of micron scale. It has not been demonstrated as yet whether control of microstructure can be extended to the nanoscale.

2.4 Sensors

The most significant property of diatoms is their biological heritage. Low-cost production of a flexible and programmable manufacturing system is possible with their self-replicate ability and possibility of genetic engineering. Immunoisolating bioencapsulation (creating biocapsules capable of protecting the enclosed tissue from immune rejection while allowing an adequate supply of nutrients and oxygen) is one of the areas that could benefit from the filtration and encapsulation properties of diatom frustules. These properties also have implications for biosensors³. Biosensors are devices incorporating a biological molecular-recognition component connected to a transducer capable of outputting a signal proportional to the concentration of the molecule being sensed¹⁶.

Gas sensors have an increasing significance because of the worsening problem of air pollution and the requirement of industry to monitor and control their environmental pollutants. Great emphasis is being given to study nano-sized semiconductor metal oxides as a sensor material since grain-size reduction and gas-diffusion control have proved to be a useful method for improving the gas sensing properties¹⁷. With decreasing crystallite size, the surface area and therefore the contribution from the surface energy to the total free energy of the system increases. This leads to high activity of materials of this kind in heterogeneous interactions. Since the geometric dimensions of nanocrystallites and molecular sizes are comparable, the kinetics of chemical transformations in nanocrystalline systems gets faster than similar processes in coarse grained crystalline materials. Therefore, nanocrystalline semiconducting oxides are very promising for development of high sensitivity, fast response gas sensors, in which surface processes play the key role in the formation of a sensor signal¹⁸.

Two types of metal oxide gas sensors can be distinguished; bulk conduction based and surface layer controlled gas sensors.

2.4.1 Bulk Conduction Based Gas Sensors

The change in bulk conductivity (σ) is a reflection of the equilibration between the oxygen activity in the oxide and the oxygen content in the surrounding atmosphere. This can be described by the following equation:

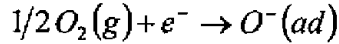
$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) P_{O_2}^{\pm \frac{1}{n}}$$

where σ_0 is a constant, E_a is the activation energy for conduction. The sign of $1/n$ depends on the type of dominant bulk defect involved in the equilibration process. A positive sign of $1/n$ means p-type conduction and a negative sign indicates an n-type conduction. Since the equation describes a conductivity characteristic common to metal oxides, virtually all metal oxides are oxygen sensors. However, in practical applications, the usefulness of a metal oxide for oxygen sensing is determined by factors such as material stability, response time, and the temperature and oxygen partial pressure range of the conductivity regime (p- or n-type conduction). Many semiconducting oxide systems have been investigated for oxygen sensor applications, notably the automotive exhaust gas oxygen (EGO) sensors for air-to-fuel ratio control. Despite their automotive application, the development of bulk conduction based gas sensors is less attractive compared to that of surface layer controlled gas sensors. First, these kinds of sensors are limited to direct monitoring of oxygen. Second, due to lack of reliability, these types of EGO sensors could not replace zirconia electrolytic type EGO sensors. The response times of bulk conduction based sensors are often slower since they rely on diffusion to change stoichiometry¹⁹.

2.4.2 Surface Layer Controlled Gas Sensors

Surface layer controlled gas sensors detect gases via variations in their resistivities. The most widely accepted explanation for this is that negatively charged oxygen adsorbates play an important role in detecting flammable gases such as H_2 and CO . In the case of n-type semiconductive metal oxides, the formation of these oxygen adsorbates builds a space-

charge region on the surfaces of the metal-oxide grains, resulting in an electron-depleted surface layer due to electron transfer from the grain surfaces to the adsorbates as follows:



The depth of this depletion layer is a function of the surface coverage of oxygen adsorbates and intrinsic electron concentration in the bulk. The resistivity of an n-type semiconductor gas sensor in air is therefore high, due to the development of a potential barrier to electronic conduction at each grain boundary, as shown in the Figure 2.

In the case of the most widely used gas sensor SnO_2 , when the sensor is exposed to an atmosphere containing reducing gases at elevated temperatures, the oxygen adsorbates are consumed by the subsequent reactions, so that a lower steady-state surface coverage of the adsorbates is established. During this process, the electrons trapped by the oxygen adsorbates return to the oxide grains, leading to a decrease in the potential barrier height and a drop in resistivity²⁰. The change in resistance is used as the measurement parameter of a semiconductor gas sensor, with sensitivity usually defined as the ratio of the resistance in air to that in a sample gas containing a reducing gas component.

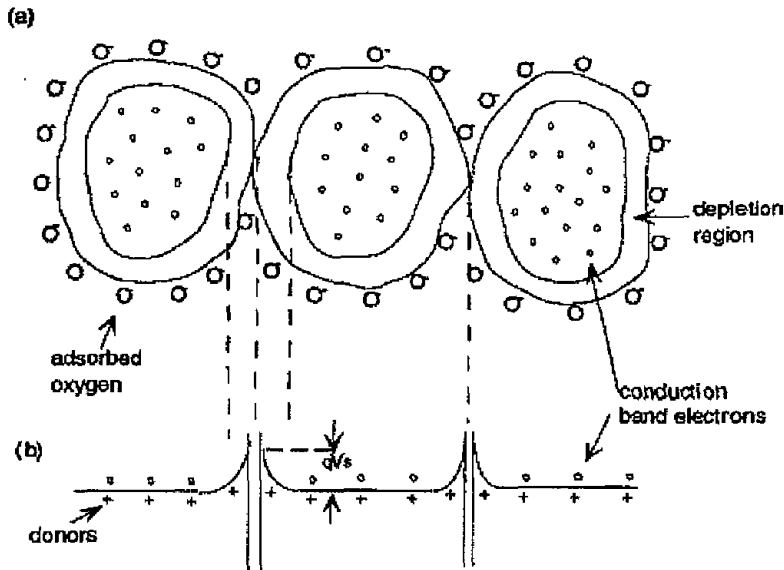


Figure 2: A model of a potential barrier to electronic conduction at a grain boundary¹⁹.

Nanocrystalline titanium oxide particles have been intensively studied due to their chemical and physical properties, which are of interest for applications such as gas sensors, catalysts, photocatalysts, pigments, optics, photovoltaic cells, and precursor materials for mesoporous materials²¹. For TiO_2 , the surface reactions tend to support a chemisorption process involving adsorption and ionization on the titania surface. An increase in electrons supplied by ionization effectively lowers the intergranular barrier height as well as the depletion region thickness¹⁹. TiO_2 sensor materials are used for detection of oxygen for air/fuel control in automobiles with their simple structure, small size and low cost²². Katayama²³ investigated Nb_2O_5 doped TiO_2 -based sensor for humidity in 1990. Humidity can be detected with the conductivity change due to proton hopping between water molecules adsorbed on the surface of TiO_2 ²⁴. Hara *et al.*²⁵ developed as a pH-sensitive electrode for use in high-temperature aqueous solutions up to 250 °C. In 1988, Shimizu *et al.*²⁶ used Ru-doped TiO_2 to sense the concentration of $(\text{CH}_3)\text{N}_3$ which increases as fish freshness decreases by Shimizu *et al.*²⁶. Lin *et al.* synthesized nanocrystalline TiO_2 to detect NO_2 and CO gases²⁷. TiO_2 has also been used for sensing H_2 gas¹⁷. A bulk controlled mechanism was proposed for H_2 sensing, in which H_2 molecules dissociate on the surface of TiO_2 , forming H atoms that diffuse into the bulk. These H atoms then ionize and produce a proton and an electron changing the conductivity of TiO_2 ^{28,29}.

2.5 Motivation

In this work we will elaborate liquid and vapor displacement reactions to convert biologically derived microscale silica into functional material compositions with shape preservation. The potential applicability of aquatic micro shells as templates for processing of nano structured smart materials will be investigated. Although not a primary objective of the work presented here, the ultimate goal of the project is to convert diatom frustules to other functional compositions to be employed as micro sensors and/or self-repairing embedded components. First, the experiment performed by Sandhage *et al.* was run to observe the results of the gas/silica displacement reaction; the reaction between magnesium

vapor and silica frustules was carried out. Then, diatom frustules were converted into TiO_2 by treating silica with TiF_4 .

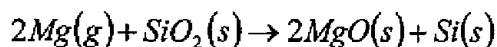
Conversion of diatom frustules into TiO_2 and its derivatives, such as BaTiO_3 , PbTiO_3 , and SrTiO_3 may lead to microscale, 3D functional components. Conversion of titania can be followed by conversion to ATiO_3 . Since the Ba-Ti-O phase diagram has several ternary compounds, it may be difficult to produce phase pure BaTiO_3 by gas-solid displacement reactions. The Pb-Ti-O and Sr-Ti-O phase diagrams have fewer ternary compounds other than PbTiO_3 and SrTiO_3 , implying that the formation of these compounds may be less problematic. The conversion series can be completed by obtaining the solid solution system $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT).

BaTiO_3 and its related compounds have been extensively used in the preparation of high permittivity capacitors, transducers and ferroelectric memories³⁰. It has also been used as gas and humidity sensors³¹⁻³³. Lead-based perovskite relaxor ferroelectrics have been investigated for their suitability in applications ranging from multilayer capacitors, transducers, to electro-optic devices³⁴. In fact not only lead-based perovskites but also the family of complex ferroelectric oxides such as BaTiO_3 , $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$, and $(\text{Ba},\text{Sr})\text{TiO}_3$ has far reaching applications in the electronics industry for transducers and actuators. Ferroelectricity is the occurrence of spontaneous polarization due to the separation of positive and negative charges in the crystal. The direction of the polarization can be defined by the application of an external field. Ferroelectric oxide nanoparticles with high anisotropic polarizability offer the possibility of taking advantage of this dielectric property in nanoscale materials science³⁵.

The solid solution system $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT), which is also ferroelectric, is now the most widely exploited of all piezoelectric ceramics. Piezoelectric materials generate an electric charge when mechanically deformed. Conversely, when an external electric field is applied to piezoelectric materials they mechanically deform. These properties enable their use in generation of high voltages, electromechanical actuators and sensors, frequency control and generation and detection of acoustic and ultrasonic energy³⁶.

2.6 Approach

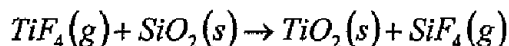
Silica frustules will react with magnesium vapor at 900°C according to the following reaction.



The Gibbs free energy of this reaction at 900 °C with $P_{Mg}=0.16$ atm is calculated to be -245.2 kJ/mol³⁷.

Volume conservation is an important criterion for shape preserving displacement reactions. According to the reaction above, one mole of silica will be converted into two moles of magnesia. Using the available data (molar volumes of silica and magnesia are 25.739 cm³ and 11.248 cm³, respectively³⁸) the volume change associated with conversion of SiO₂ to MgO is -12.6%. The products of the reaction, MgO and Si, are mutually insoluble and Si may be removed from the system with suitable etchants.

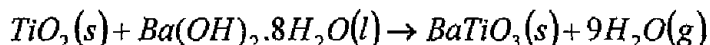
After conversion of silica to magnesia, the conversion of silica to titania was studied. The reaction;



is thermodynamically favored with $\Delta G = -75.4$ kJ/mol at 330 °C. The data indicates that the volume change will be -20.3% (molar volume of titania is 20.522 cm³).

The review of potential reactants and thermodynamic data indicated that one-step conversion of frustules into ATiO₃ (A=Ba, Pb, Sr) is not practical. Instead, conversion of silica to titania followed by reaction of titania to form ATiO₃ was thought to be a more promising route.

The reaction of conversion of titania frustules into BaTiO₃ was carried out with Ba(OH)₂.



which has a Gibbs free energy of -61.2 kJ/mol at 120 °C. The reaction temperature was around 120 °C, which is about 40 °C higher than the melting temperature ($T_m=78$ °C) of Ba(OH)₂·8H₂O.

3 EXPERIMENTAL PROCEDURES

3.1 Materials

Diatomaceous earth was purchased from a local supplier (Glorious Gardens, Inc., Des Moines, IA). The chemical composition of the pyrolyzed frustules were determined by wet chemical analysis (NSL Analytical Services, Inc., Cleveland, Ohio) and found to consist of 92% SiO_2 , 3.34% Al_2O_3 , 1.16% Fe_2O_3 , 1.11% CaO , 0.7% Na_2O , 0.52% MgO and 0.46% K_2O . Before displacement reaction experiments, small and broken pieces were eliminated by sedimentation of the frustules. First, a suspension of the frustules was prepared and allowed to settle out of the suspension. Decantate containing small or broken frustules were poured out. This procedure was repeated several times then the final sediment was placed in an oven to dry. The results are shown in Figure 3.

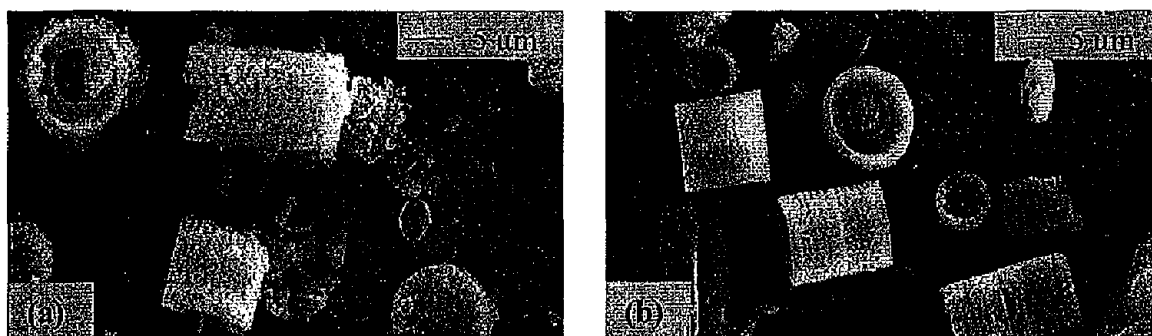


Figure 3: Scanning electron micrographs of diatomaceous earth frustules. (a) natural frustules, and (b) frustules after sedimentation to eliminate small pieces.

3.2 Conversion of Diatoms to MgO

Recently, Sandhage and his co-workers have demonstrated the conversion of diatom frustules to MgO ². The objective of the preliminary experiments presented in this work is to verify that silica-based diatom frustules can be converted into MgO and to build on this experience by forming new compositions through displacement reactions. The shape-preserving, chemical conversion process is done by treating SiO_2 -based diatom frustules

with Mg vapor to produce MgO. This experiment requires a sealed reactor and a temperature higher than the melting point of Mg that is 649 °C.

The experiment consists of two steps. First, the silica frustules (diatomaceous earth) were heated to 600 °C for 8 hours in air to pyrolyze the organic contaminants that may be present in the sample. Then, the pyrolyzed frustules (the experiments were carried out with different amounts of frustules from 50 to 250 milligrams) were transferred into the sample holder. The frustule-containing sample holder consisting of a stainless steel platform with two cavities, one containing frustules and the other containing Mg chunks (magnesium metal-turnings for grignard reaction, >99, Fisher Chemicals), was placed in a steel tube, as shown in Figure 4 (a). The amount of magnesium used for the experiments ranged from 80 to 400 milligrams. Experiments were carried out at various ratios of reactants and with varying total mass of reactants. The reactor tube was threaded at one end, which was sealed with a bolt using carbon black as lubricant.

The experiments were run at a temperature range from 750 to 900 °C and dwell times were changed from 0.5 to 4 hours. The reactor was kept under a blanket of flowing argon gas to prevent oxidation of the steel tube at elevated temperatures. A gas flow meter was used to control the Ar flow, and a gas bubbler was attached to prevent backflow of oxygen into the tube. After cooling to room temperature, the reacted frustules were removed from the steel reactor.

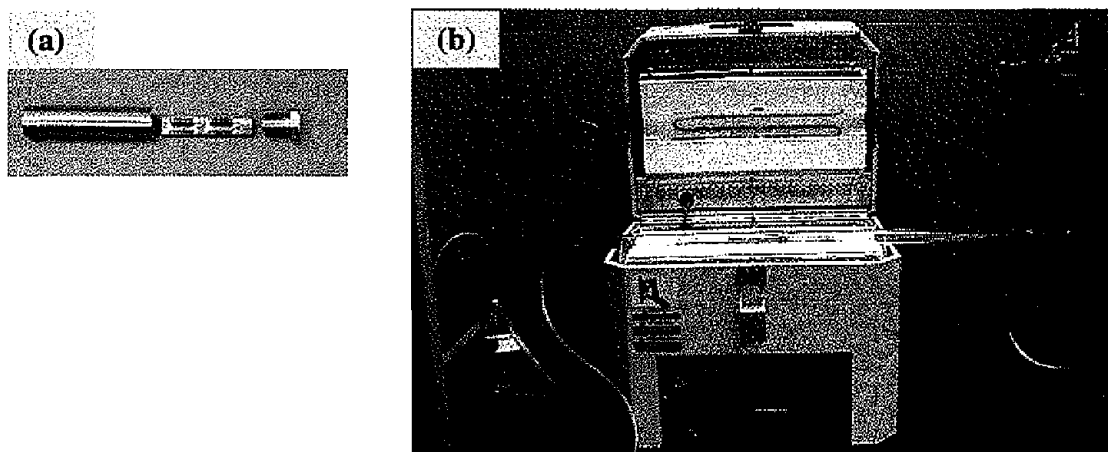


Figure 4: (a) The stainless steel reactor and the sample holder. (b) Experimental setup used for conversion of diatomaceous earth to MgO. The sealed stainless reactor kept in argon blanket to prevent oxidation.

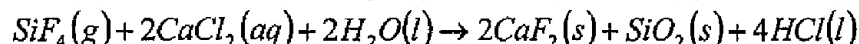
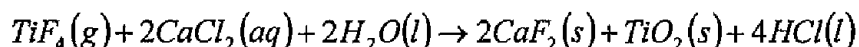
3.3 Conversion of Diatoms to TiO_2 and $BaTiO_3$

3.3.1 Conversion to TiO_2

Conversion of silica frustules into TiO_2 can be summarized by the following chemical reaction:



TiF_4 (Titanium (IV) fluoride, 100%, Alfa Aesar) and pyrolyzed frustules were placed on the base (Figure 5(d)) of the reactor (Figure 5(c)) in an argon-filled glove box. Titanium fluoride is toxic and it should be handled under dry protective gas, therefore a glove box, with an atmosphere maintained at a low oxygen and moisture level with a purifying system, was used. The reactor was sealed using a high vacuum silver coated copper gasket and the valves were closed before removing from the glove box. For every experiment a new gasket was used to provide a gas tight seal. The reactor was placed into the crucible furnace (Figure 5(a)) inside the fume hood, and the gas inlet valve was connected to an Argon cylinder. The gas supply line was purged prior to connecting to the reactor to eliminate contact of TiF_4 with air. An exit valve and a pressure relief valve were connected to the scrubber containing a saturated $CaCl_2$ solution. In the event of gas pressure build up ($P > 10$ atm) the gas would be released to the scrubber. The sublimation temperature of TiF_4 is $284\text{ }^\circ\text{C}$ ³⁸; therefore to be able to run a gas-solid reaction, the temperature of the experiment must be higher than $284\text{ }^\circ\text{C}$. The O-ring of the inlet and exit lines withstand up to $350\text{ }^\circ\text{C}$; so the reactor was heated to $330\text{ }^\circ\text{C}$ at a rate of $5.5\text{ }^\circ\text{C/min}$. Heating tape was used to heat the exit line to prevent the condensation of unreacted TiF_4 at the end of the experiment. At the end of the desired reaction time, argon was flushed through the reactor to purge the gaseous by product SiF_4 , which is also toxic, and unreacted TiF_4 while it was still in the gaseous form. Gaseous SiF_4 and TiF_4 were bubbled through the $CaCl_2$ solution. Any unreacted TiF_4 gas reacts with aqueous $CaCl_2$ and forms TiO_2 and CaF_2 ; similarly gaseous SiF_4 forms SiO_2 and CaF_2 upon reaction with aqueous $CaCl_2$ as shown in the following chemical reactions.



The furnace was then cooled to room temperature. The valves were closed, and the product was placed in a sealed vial for characterization.

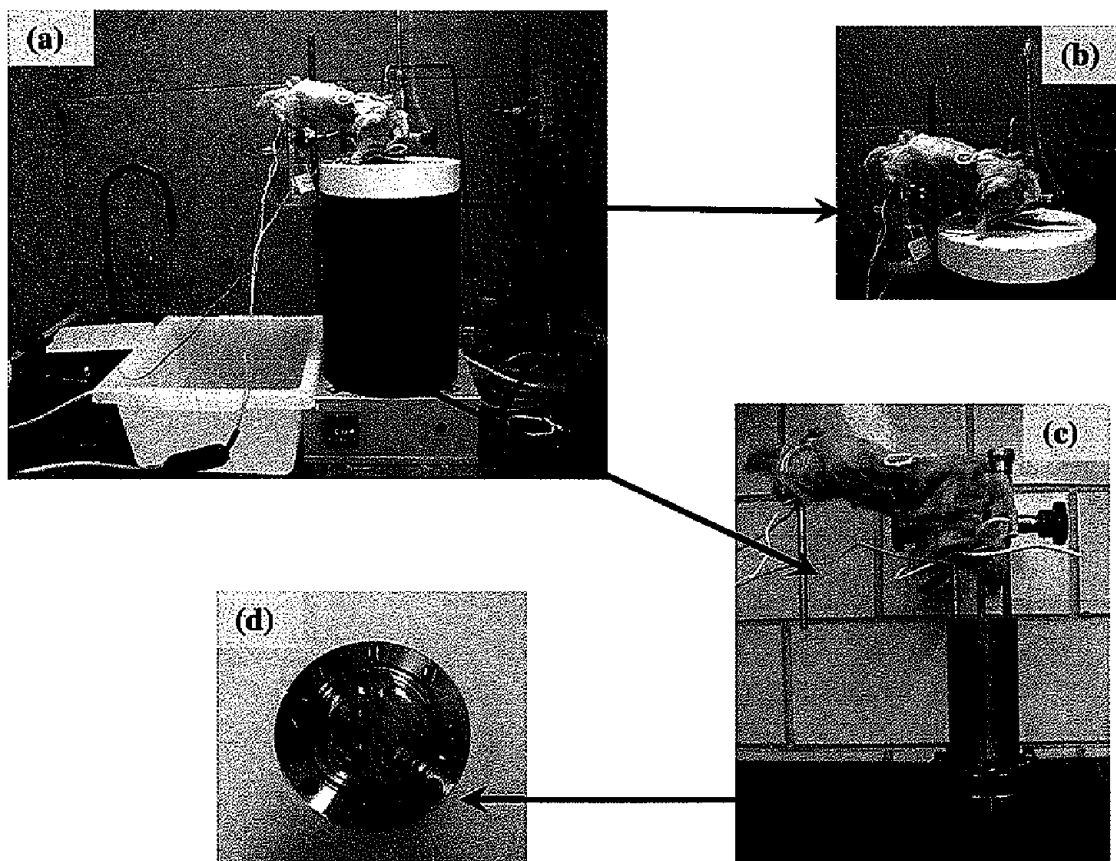
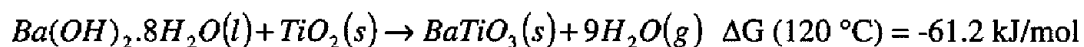


Figure 5: (a) Experimental setup used for conversion of diatomaceous earth frustules to TiO_2 . A crucible furnace is used for the experiment. (b) Three valves of the reaction cell which are wrapped with heating tape and the scrubber. (c) The reaction cell. (d) The base of the reactor. The reactants, diatomaceous earth frustules and TiF_4 , were placed in separate cavities of the reactor. Gasket is used for sealing the base to the reactor body.

3.3.2 Conversion to BaTiO_3

The reactions carried out to convert titania frustules into BaTiO_3 can be written as:



Since the Ba-Ti-O phase diagram has several ternary compounds, it may be difficult to produce BaTiO_3 with a gas/solid reaction. It was also found that melting points of the

oxides are very high to use in shape preserving reactions. It is likely that the conversion of SiO_2 by gas phase reaction to TiO_2 followed by conversion to BaTiO_3 via a solid/liquid reaction is more promising.

$\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ (Barium Hydroxide Octahydrate, >98%, Fisher Chemicals) and titania frustules were put into a crucible and reaction was carried out with a solid-liquid reaction. The experiments were conducted at different temperatures ranging from 95 to 850 °C for different times (2 to 6 hours) with different conditions, i.e. in crucible, in sealed reaction chamber, loaded under argon atmosphere. After the experiment, unreacted barium hydroxide has to be removed from the sample. Water was added to dissolve unreacted Ba(OH)_2 and the solution was filtered.

3.4 Characterization

Natural diatomaceous earth frustules before and after reactions were analyzed with scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and powder X-ray diffraction (XRD) methods. Wet chemical analysis was employed to determine the compositions of the frustules quantitatively. Details of the frustule features were examined with SEM before and after reaction. Elemental constituents of the frustules were determined by EDS. Structural characterization of the frustules was performed with XRD. Crystallite sizes of the frustules were also calculated using this data. Grain sizes and selected area diffraction (SAD) patterns of the reacted frustules were determined by transmission electron microscopy (TEM). Since the gas sensing properties are surface sensitive, surface area is a very important parameter for the materials that are sensor candidates. BET surface area measurements were made using 11-point Nitrogen gas adsorption at liquid N_2 temperature and applying the BET method to determine the specific surface area of frustules.

4 RESULTS & DISCUSSION

4.1 Conversion to MgO

Scanning electron micrographs of the frustules before and after the reaction at 900 °C for 4 hours indicate that the overall frustule shape and microscale features were retained following the reaction.

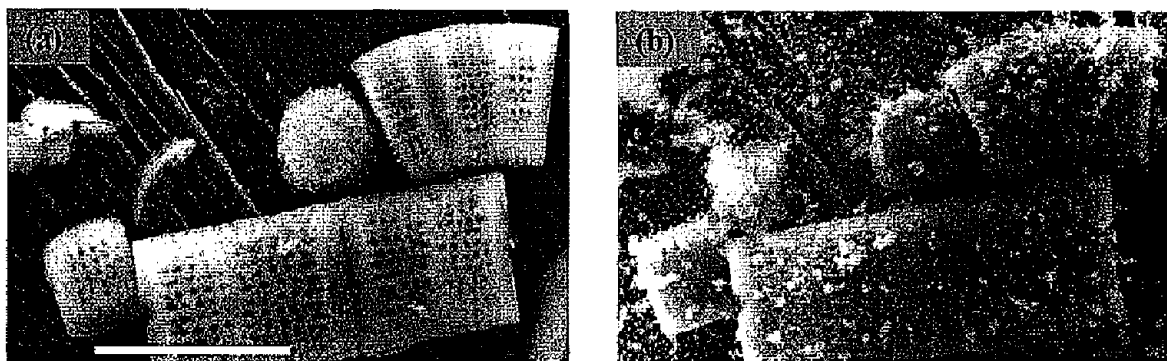


Figure 6: Scanning electron micrographs of (a) frustules before reaction and (b) after reaction. By looking at the product it can be inferred that the shape and details of the frustules were retained after reaction. The scale bar indicates 20 μm .

The X-ray diffraction pattern of natural diatomaceous frustules confirmed that the as received diatomaceous earth is indeed mostly amorphous silica as evidenced by a weak, broad peak around $2\theta=20^\circ$ as shown in Figure 7a. For comparison an XRD pattern of amorphous silica from Alemany³⁹ is also given in Figure 7b. Small sharp peak around $2\theta=35^\circ$ is believed to be due to crystalline albite ($\text{NaAlSi}_3\text{O}_8$). After pyrolysis, the organic material is burned off but the sample is still amorphous as indicated by an XRD pattern (not shown) similar to the as received frustules. The powder X-ray diffraction pattern of the reacted frustules revealed MgO along with elemental Si, produced by the reaction (Figure 8). The sharp and high intensity of the peaks indicates that MgO produced under these experimental conditions is well crystallized and crystallite size appears to be on the order of tens to hundreds of nanometers as expected from high reaction temperature and long time employed for this reaction.

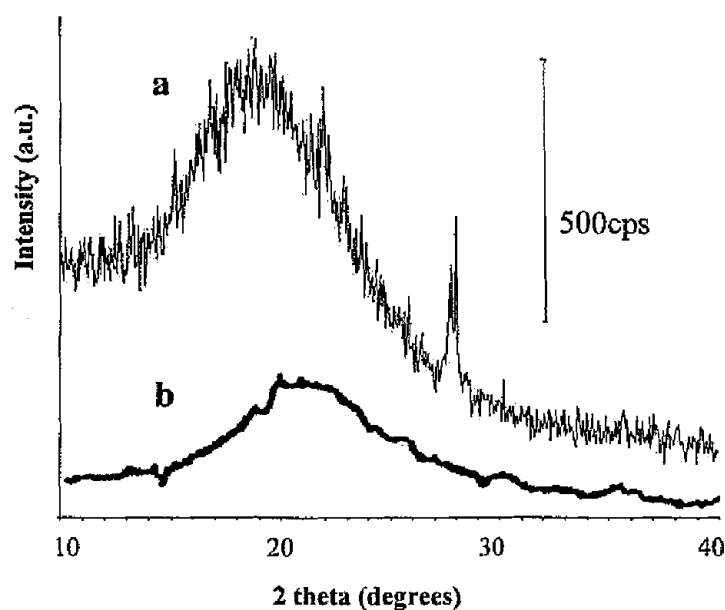


Figure 7: XRD pattern of as received frustules after pyrolysis (a). XRD pattern of amorphous silica from literature (b)³⁹. The peaks belong to crystalline albite can be seen in the pyrolyzed diatoms.

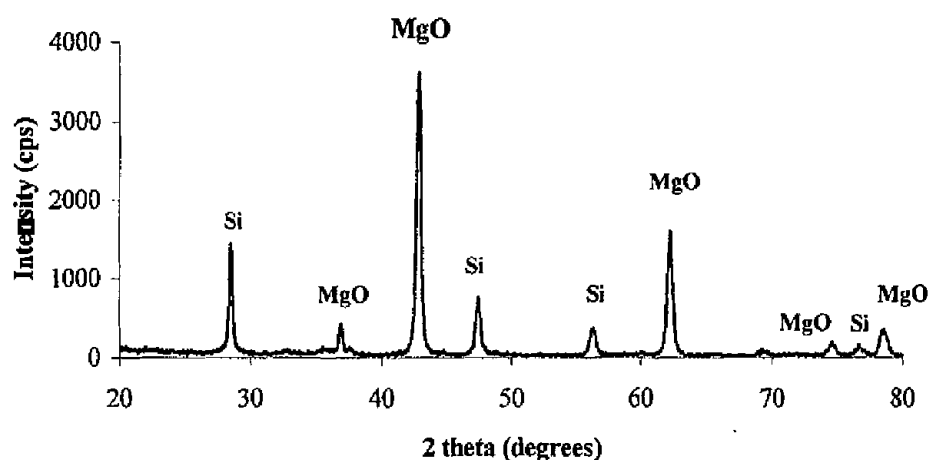


Figure 8: XRD pattern of frustules after reacting with Mg vapor at 900°C for 4 hours.

Chemical constituents of the reacted frustules were determined using energy dispersive spectroscopy (EDS). The EDS analysis shows magnesium, oxygen and silicon peaks (Figure 9). Energy dispersive spectrum reveals the elemental constituents of the frustules yet the technique can not able to discriminate elemental Si from unreacted silica;

therefore we cannot use this method to decide about the nature of the silicon peak. However, XRD pattern of the reacted frustules provides a strong support for the absence of unreacted silica. As discussed above, as received frustule is amorphous, but after 4 hours at 900 °C only crystalline MgO and Si were observed. No evidence of either crystalline or amorphous silica was found in XRD pattern of reacted frustules. Furthermore, the frustules were pyrolyzed at 1000 °C for 12 hours, so the material would be completely crystallized as shown in Figure 10(a). Then, to confirm that all the frustules reacted, crystallized frustules were used in the experiment. The powder X-ray diffraction pattern showed the MgO and Si peaks but no SiO₂ peaks were observed (Figure 10b). This experiment further confirmed that all the frustules reacted with Mg in the above experiment.

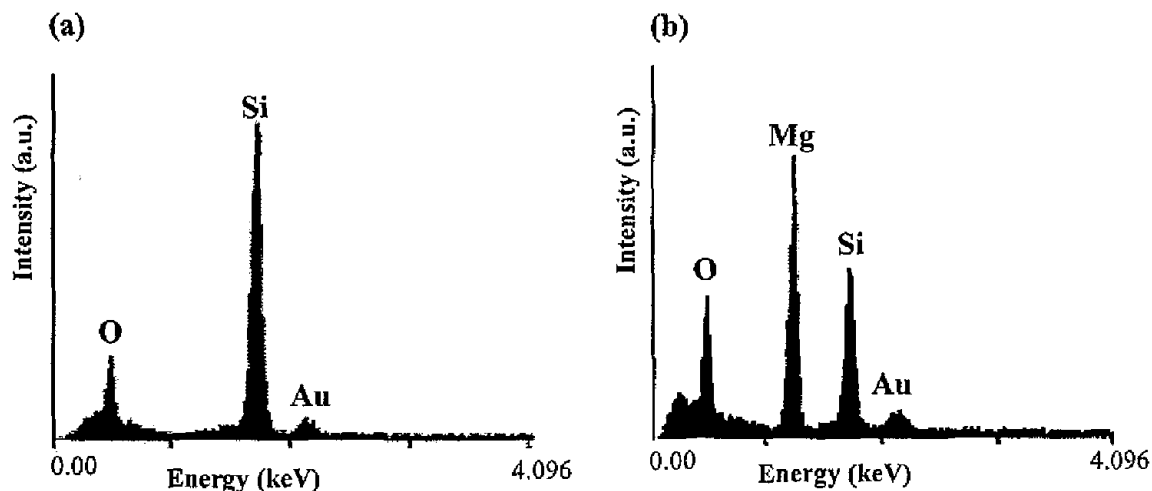


Figure 9: Energy dispersive spectrum (EDS) of (a) natural diatoms frustules and (b) reacted diatom frustules. As expected, two major peaks, Mg and Si, were observed after the reaction. Note the small Au peak is due to gold coating in order to avoid surface charging.

The completion of the reaction was also verified by wet chemical analysis. The analyses results are shown in Figure 11. The calculations showed that while 100% of the frustules converted into MgO at the end of the reaction at 900 °C for 4 hours, conversion percentage decreased to 85% at 800 °C and 44% at 750 °C (The calculations are shown in the appendix).

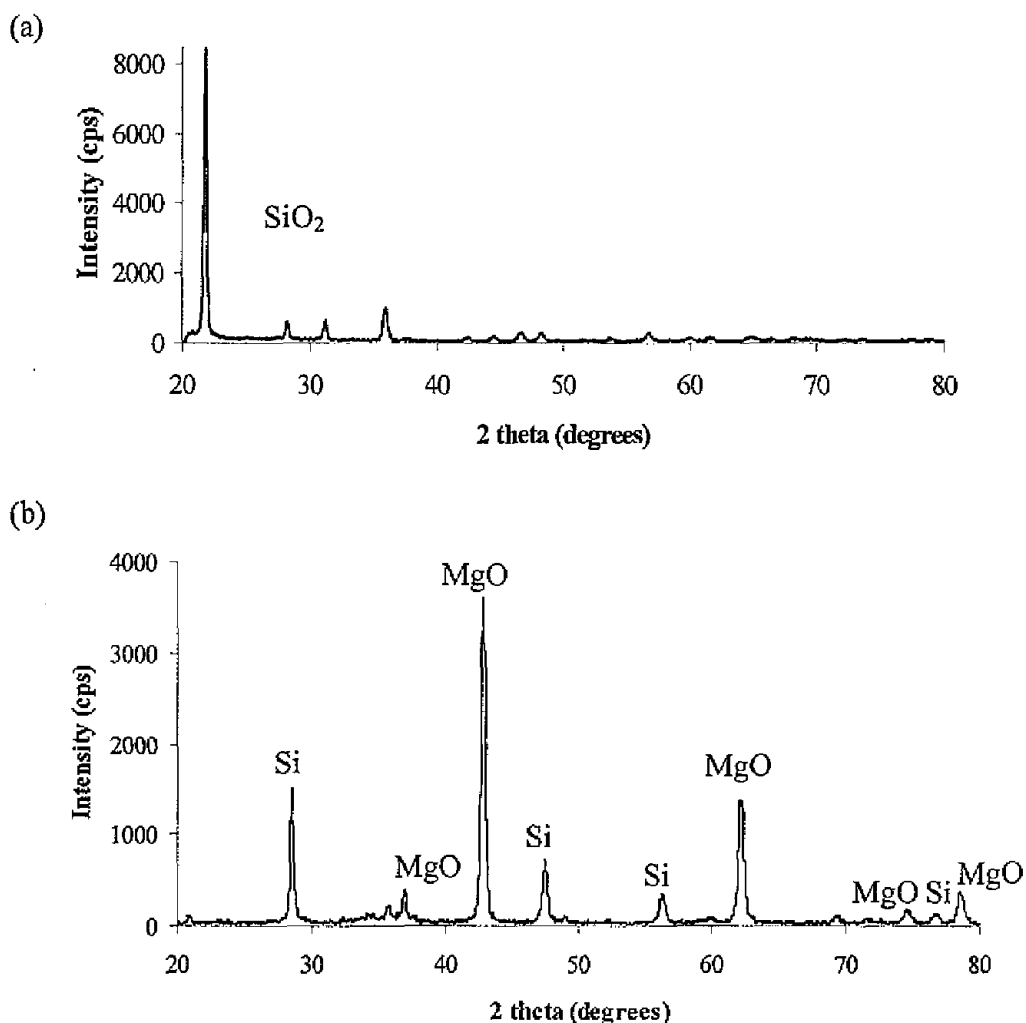


Figure 10: XRD of diatoms (a) heated to 1000 °C and held at that temperature for 12 hours. After the heat treatment, amorphous background disappears and, sharp well crystallized cristobalite SiO₂ peaks are observed. (b) after reaction. Practically all the major peaks were assigned to MgO and Si. No SiO₂ peak was observed.

	Natural	Pyrolyzed	900 °C	800 °C	750 °C
MgO	0.5	0.5	74.6	62.2	39.5
Si	43.3	42.9	22	24.3	30

Figure 11: The weight percentages of MgO and Si in the natural, pyrolyzed, and reacted frustules determined by wet chemical analyses.

The calculations show that the conversion percentage decreases as temperature decreases. The change of the rate of the overall reaction due to the reaction temperature would affect the conversion. The rate equation can be written as:

$$r = ka_{\text{SiO}_2} P_{\text{Mg}}^2$$

In this relation, the concentration of silica was represented with its activity and concentration of magnesium indicated as the vapor pressure of magnesium. The rate constant k depends strongly on temperature, obeying Arrhenius Law¹⁰.

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right)$$

The vapor pressure of magnesium in the reaction cell is also affected by the reaction temperature. The vapor pressure of magnesium at 900 °C is 0.16 atm³⁷. At 800 °C this value decreases to 0.05 atm, and at 750 °C decreases down to 0.02 atm. Although the rate of the reaction is fast enough for the complete conversion at 900 °C in several hours, apparently the reaction rate is too slow for complete conversion at lower temperatures.

Particle size has a significant effect on mechanical, electronic, magnetic and optical properties of a material. By varying the reaction temperature and time, the crystallite size and surface area can be selectively tailored within a range.

Crystallite sizes of the reacted frustules were calculated using the (200) diffraction peak of MgO and employing the Scherrer formula, $D=0.9\lambda/(\beta\cos\theta)$, where D is the crystallite size, λ is the wavelength ($\text{CuK}\alpha$), β is the true peak broadening expressed as full-width at half maximum, and θ is the diffraction angle. The instrumental broadening was determined with LaB_6 scan and the crystallite size of frustules reacted at 900 °C for 4 hours was calculated as 27.2 ± 1.2 nm. As expected the crystallite size decreased with decreasing temperature and time. Figure 12 shows the effect of time and temperature on the measured crystallite size.

As time and temperature increases, crystallite size increases, but as it is seen in the figure, temperature has a dominant role. The crystal size increase can be expressed with the formula:

$$D^2 = D_0^2 + Kt$$

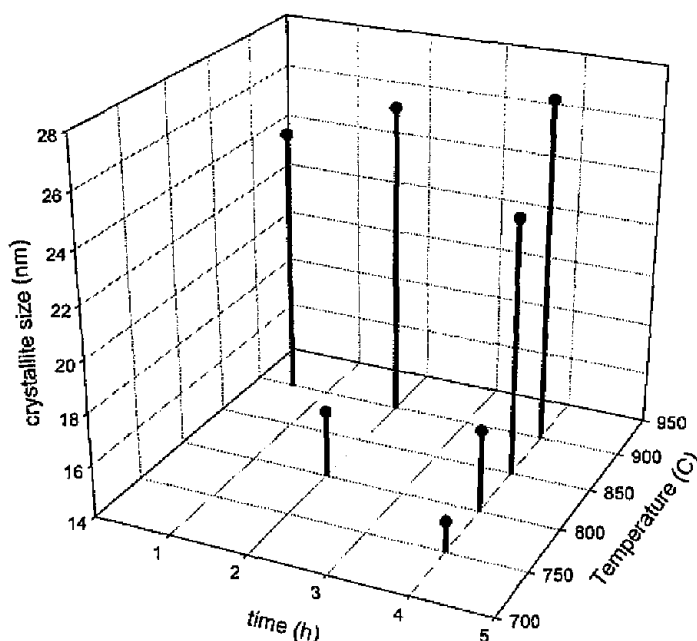


Figure 12: Effect of time and temperature on crystallite size. The effect of temperature on crystallite size is quite significant while the effect of time is much weaker.

In the formula, D_0 is the grain diameter at time $(t) = 0$, and $K = 4\alpha M\gamma$. α is a proportionality constant on the order of unity and γ is the interfacial free energy, M is mobility of the grain boundary, i.e. velocity under unit driving force, and exponentially increases with temperature. This exponential increase in the mobility term makes temperature the dominant factor in grain size change⁴⁰.

The TEM analysis of the frustules reacted at 900 °C for 4 hours was done with crushed frustules. The crystallite size was also calculated with TEM micrographs. The value was determined as 39 ± 19 nm. The selected area diffraction (SAD) pattern acquired from a reacted frustule showed ring pattern of MgO.

For sensor applications, high surface area is an important materials property. High surface area is one of the unique features of diatoms. A number of measurements have been performed showing that the specific surface area differs among and even within species. *Thalassiosira descipiens* is the diatom that had been reported to have the highest measured specific surface area as $258 \text{ m}^2/\text{g}$ ⁵.

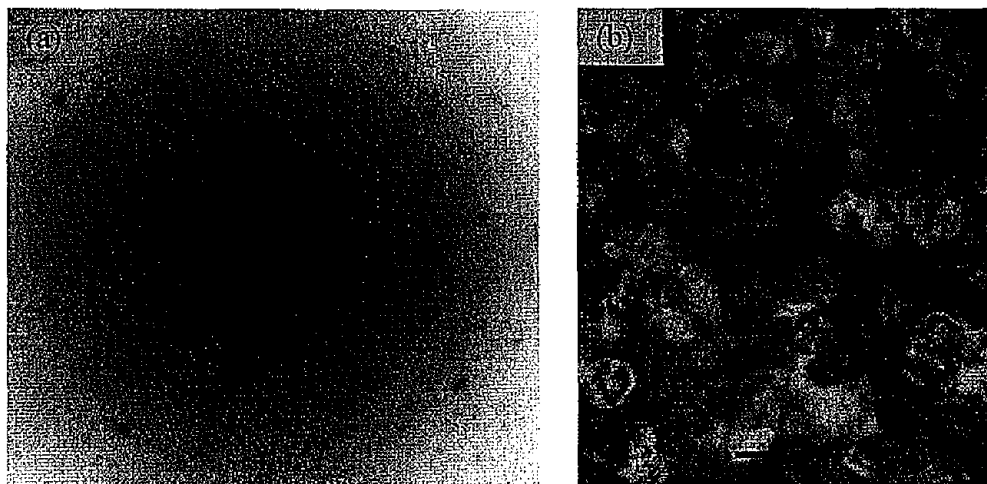


Figure 13: TEM analysis indicated the crystallite structure of the reacted frustules was magnesia (a) and crystallite size was around 40 nm (b).

Although diatomaceous earth consists of diatom frustules, the amorphous native particles may differ in various respects. The specific surface area of diatomaceous earth was reported as $22 \text{ m}^2/\text{g}$ ⁷. In our laboratory, nitrogen adsorption isotherm experiments were conducted (Quantachrome Corporation, Autosorb 1, Gas Sorption System) to measure the specific surface area of the frustules. BET surface area of the natural frustules was measured as $29 \text{ m}^2/\text{g}$. After heat treatment at $400 \text{ }^\circ\text{C}$ for 8 hours, this value increased to $30 \text{ m}^2/\text{g}$. Following heat treatments at $600 \text{ }^\circ\text{C}$ and $800 \text{ }^\circ\text{C}$ for 8 hours resulted in $26 \text{ m}^2/\text{g}$ and $23 \text{ m}^2/\text{g}$, respectively⁴¹. Goren *et al.*⁴² also observed a decrease in surface areas of the heat treated frustules. The change in surface area with temperature is not dramatic, it is reasonable. In many hydrated materials the surface area values go through a maximum when measured as a function of temperature. At modest heat treatment temperatures ($400 \text{ }^\circ\text{C}$) the evolution of chemisorbed gases and dehydroxylation of the surface leads to an increase in surface area. Yet at higher temperatures, the surface area decreases due to sintering and grain growth.

Specific surface area of the frustules reacted at $900 \text{ }^\circ\text{C}$ for 4 hours is determined to be $5 \text{ m}^2/\text{g}$. This value increases to 7 and $11 \text{ m}^2/\text{g}$ when the reaction takes place at 800 and $750 \text{ }^\circ\text{C}$, respectively. Comparison of specific surface area of reacted frustules to the frustules just heat treated at similar temperatures show that the surface area of reacted

frustules is significantly smaller than the heat treated ones. It is plausible that the diffusion is faster for MgO than SiO₂ at similar temperatures.

The total mass of the reactants as well as molar ratio of reactants, i.e. $n_{\text{Mg}}/n_{\text{SiO}_2}$ had a pronounced effect not only on the extent of the reaction but also on the kind of phases formed. For instance, when the Mg content was high, reaction product included significant amount of Mg₂Si as indicated by the XRD patterns. The effects of time and temperature were also investigated in the experiments that were carried out with different Mg to SiO₂ molar ratios and total mass values. Figure 14 shows the XRD diffraction patterns of reacted frustules at 900 °C at several reaction times. Figure 15 shows XRD patterns of two samples reacted at 800 and 900 °C for 4 hours.

As it can be seen, the XRD patterns of the samples include Mg₂Si peaks. This might have been formed during solidification of the molten Mg-Si products of the reaction². In addition to time and temperature, both the ratio and total amount of reactants were varied to see the effects of these parameters on Mg₂Si formation. The results of these experiments are

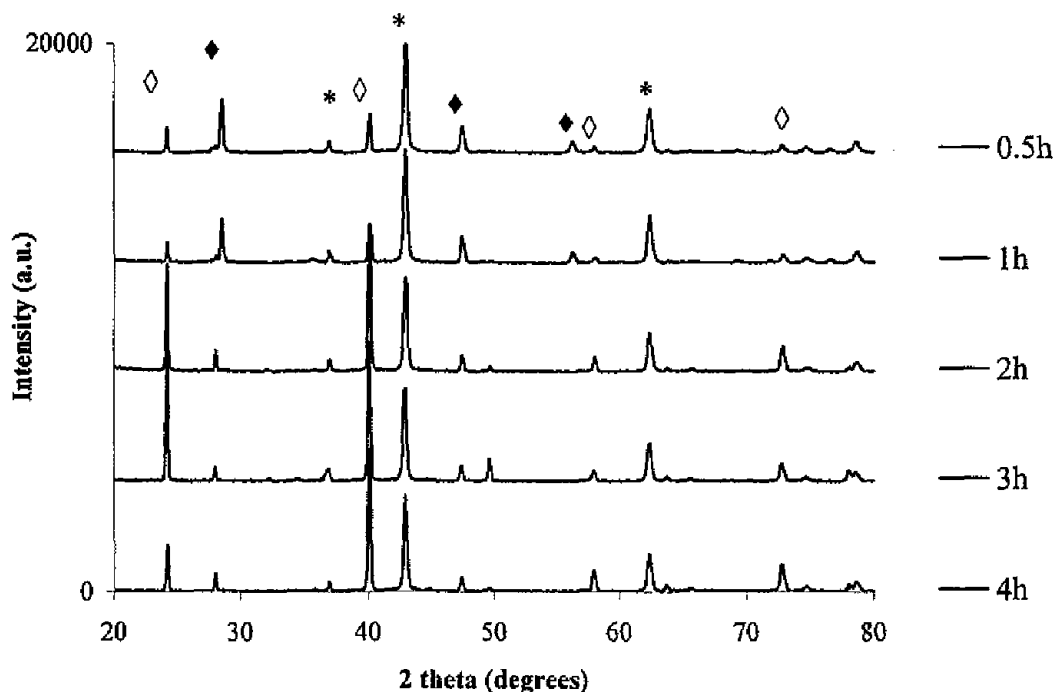


Figure 14: XRD pattern of frustules after experiments with different reaction times at 900 °C. * indicates the MgO peaks, ♦ indicates Si peaks and ◇ indicates Mg₂Si peaks.

summarized in the following figures. Excess Mg is calculated by subtracting the sum of the amounts of Mg that satisfies the saturation Mg vapor pressure inside the reaction tube and Mg that reacts with silica from the amount of Mg in the reaction tube. The extent of Mg_2Si formed is expressed by normalizing against the MgO phase formed by taking the ratio of most intense peak of Mg_2Si to the most intense peak of MgO.

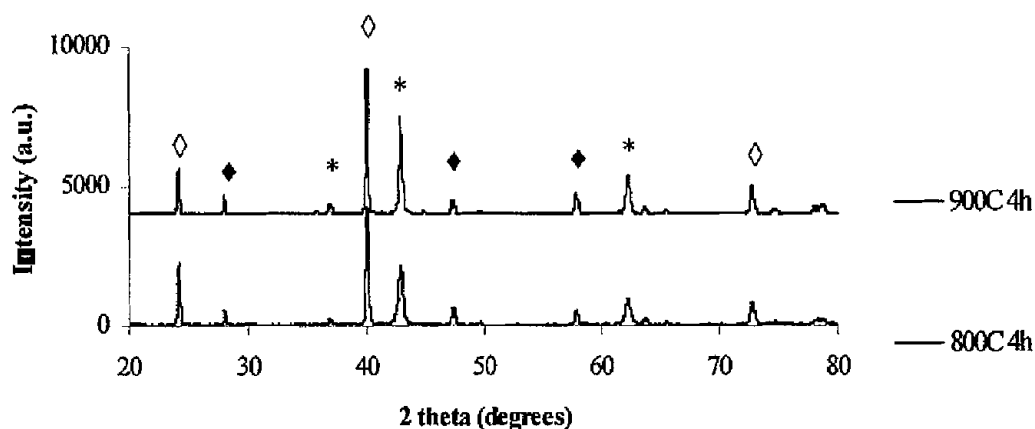


Figure 15: XRD pattern of frustules after experiments with different reaction temperatures. * indicates the MgO peaks, ♦ indicates Si peaks and ◇ indicates Mg_2Si peaks.

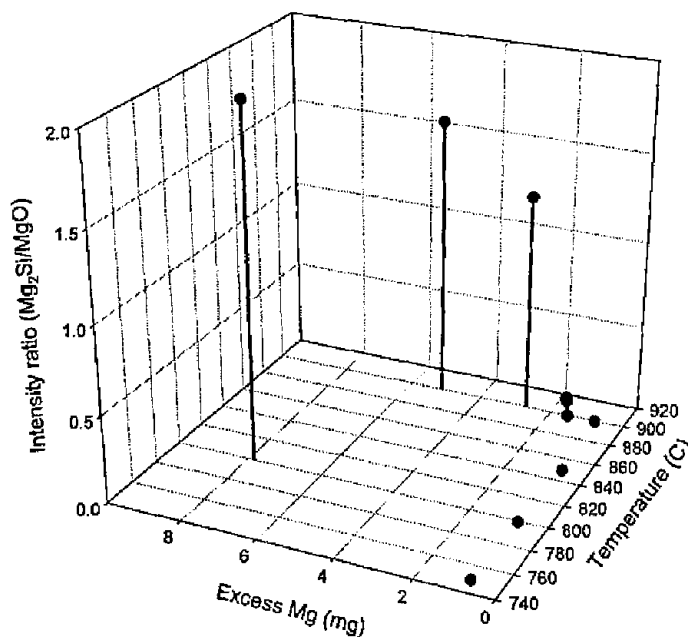


Figure 16: Effects of temperature, amount of excess magnesium in the reaction cell and formation of Mg_2Si on crystallite size.

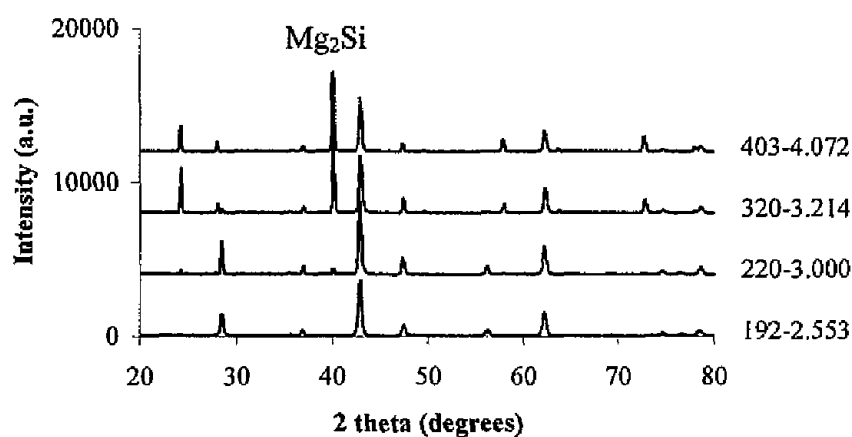


Figure 17: XRD pattern of reacted frustules with different total mass of reactants (mg) - Mg/SiO_2 molar ratios, as indicated. The experiments were carried out 900°C for 4 hours.

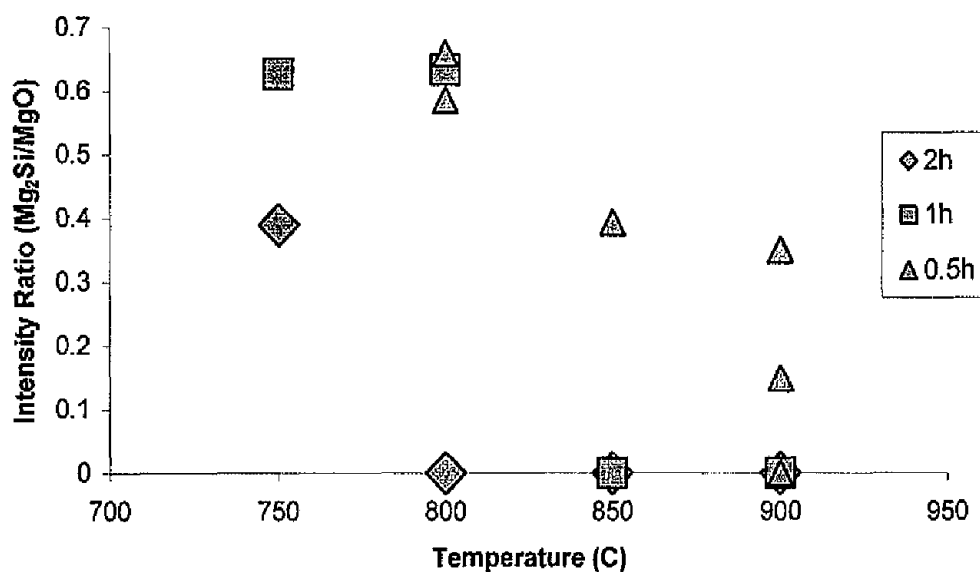
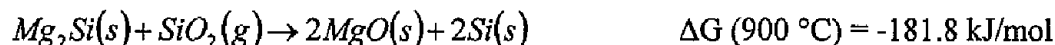
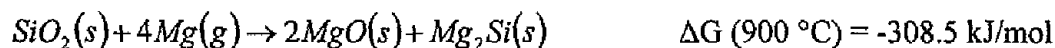


Figure 18: Effect of temperature on formation of Mg_2Si for 2, 1, and 0.5 hours experiments. Amount of excess magnesium kept below 2 milligram.

The figure 16 shows how the formation of Mg_2Si is affected by the excess Mg and reaction temperature. According to the plot as excess magnesium decreases, produced Mg_2Si decreases and vanishes. This phenomenon is also shown with the XRD pattern in Figure 17.

The intensity ratio versus temperature plot was drawn for different times at 0 to 2 milligram excess magnesium range. It can be seen that as time decreases, Mg_2Si begins to form even at higher temperatures. For example, experiments that were run for 4 hours with the excess Mg that is less than 2 mg do not have any Mg_2Si in that range regardless of the temperature (Figure 16). However, in two-hour experiments, the Mg_2Si was formed at 750 °C, and in 0.5 hour experiments, Mg_2Si formed even at 900 °C (Figure 18). Mg_2Si might be forming initially and decreasing with time. A plausible reaction path that explains formation of Mg_2Si in the early stages and disappearance at the later stages of the process is given by the following chemical reactions.



Of course, if there is excess Mg in the chamber it may form at the expense of elemental silicon, the reaction by product, as illustrated by the following reaction:

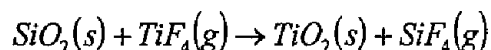


The experiments presented above confirmed the findings of Sandhage and his coworkers that gas/solid reactions can be used to convert complex-shaped, frustules into magnesia that retain the shapes and fine features of the starting preforms². In addition, the present work highlighted the role of each of the experimental condition including temperature, reaction time and reactant ratio. Conditions leading to complete conversion and phase-pure product while retaining the frustule morphology were also elucidated.

4.2 Conversion of Diatoms to TiO_2 and $BaTiO_3$

4.2.1 Conversion to TiO_2

The benchmark experiment to convert SiO_2 frustules to TiO_2 were carried out at 330 °C for 1 hour in a sealed reaction chamber. The expected overall chemical reaction for the conversion is given below:



For this experiment, the molar ratio of TiF_4 to SiO_2 was 2.5.

Scanning electron micrographs of the frustules before and after the reaction indicate that overall shape of the frustules is retained and are shown below (Figure 19). Although it is observed that most of the frustules preserve the fine features, the frustules seemed more granular compared to natural frustules (Figure 19c). The elemental analysis by energy dispersive spectroscopy (EDS) shows high intensity Ti and F peaks after the reaction.

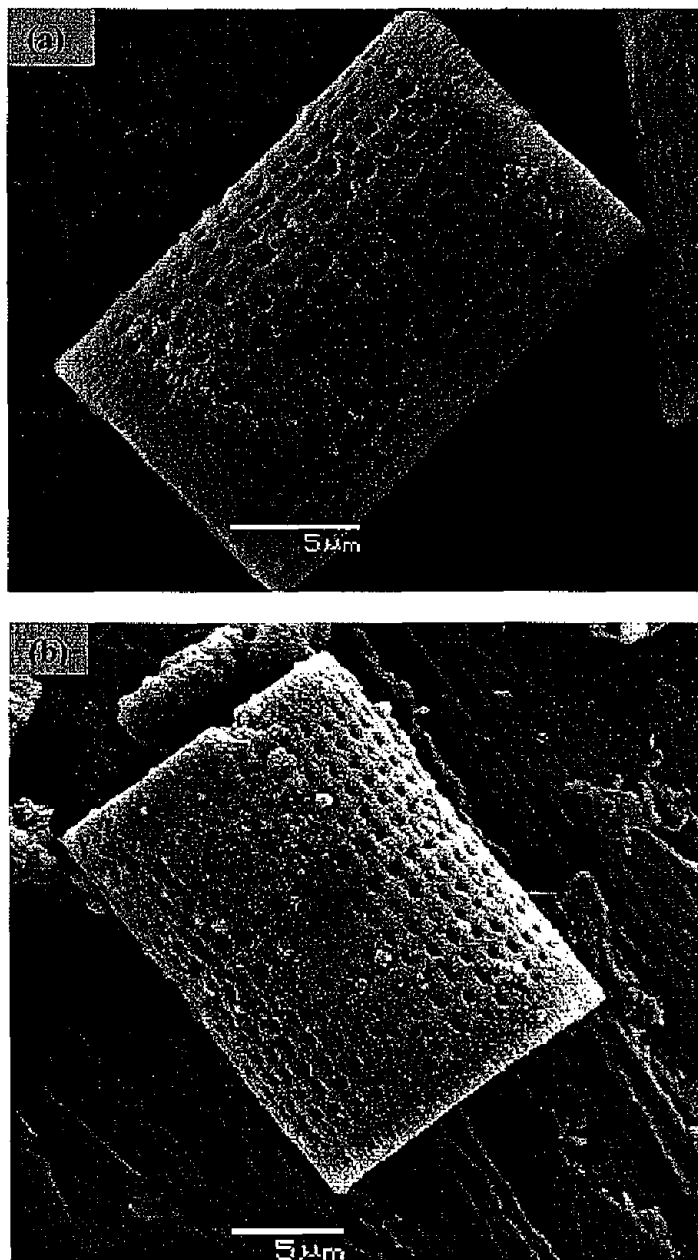
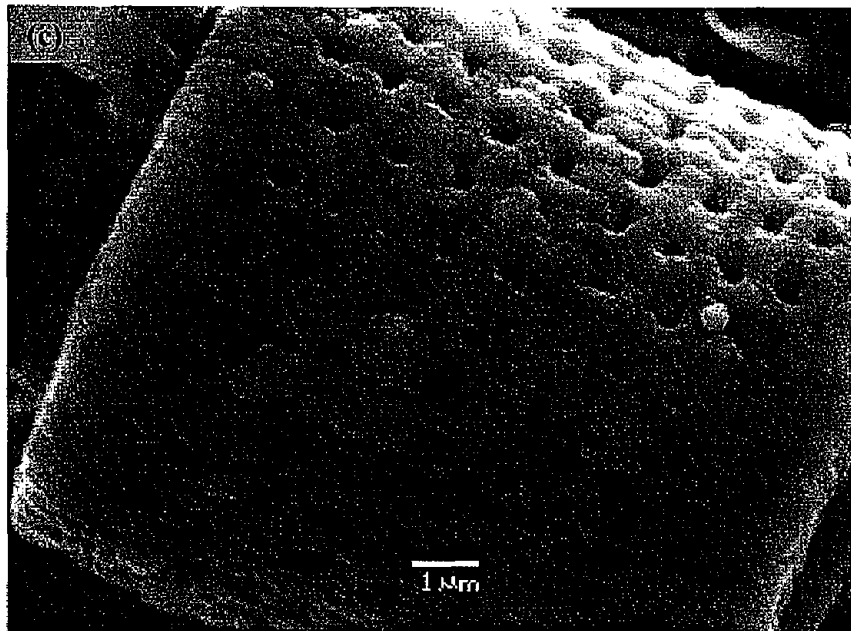


Figure 19: The SEM micrographs (a) before and (b) after the reaction.



(d)

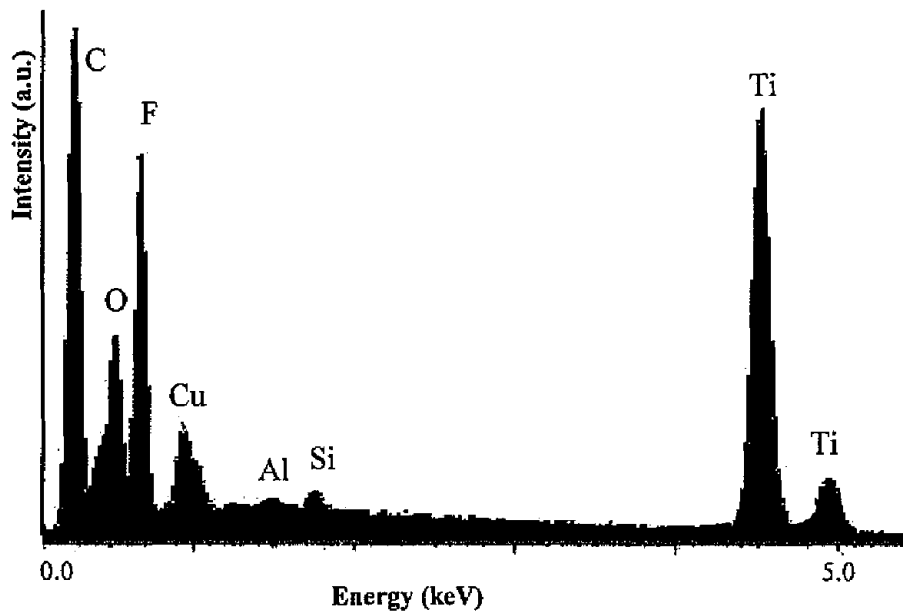
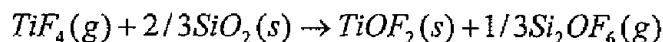
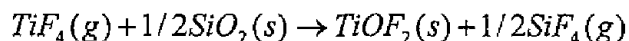
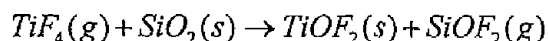


Figure 19 (continued): (c) It was observed that some frustules have more granular morphology. (d) The EDS spectrum includes Ti peak and high amount of F. High carbon peak due to carbon coating, and Cu peak due to Cu sample holder can be seen. The reacted frustule still includes small amount of Si.

The powder X-ray diffraction pattern of the reacted frustules (Figure 20a) reveals that the frustules were converted into TiOF_2 . Possible reactions that could convert silica frustules into TiOF_2 are⁴³:



Although the standard Gibbs free energy is less negative than the reaction written above, the following reaction also would convert frustules into TiOF_2 .



TiOF_2 frustules are converted into TiO_2 via further heat treatment at 600 °C for 3 hours in air. XRD pattern of the reacted frustules (Figure 20b) verified that they were converted into anatase which is one of the three crystallographic forms of TiO_2 . The other two are brookite, and rutile. Rutile is the thermodynamically most stable form and although the others are kinetically stable, they will convert to rutile phase irreversibly. The transformation temperature range from anatase to rutile varies from 400 °C to 1200 °C, depending on the method of synthesis, the atmosphere, and the presence of foreign ions. The overall effect of impurities appears to be twofold. First, impurities raise the transformation temperature. Second, the nature of the impurities appears to control the stoichiometry of the TiO_2 and thus the oxygen vacancy concentration. Ions of valence less than four and of small ionic radius which can substitutionally enter the structure would be expected to increase the oxygen vacancy concentration. This increase in vacancy concentration presumably reduces the strain energy which must be overcome before rearrangement of the structure can occur. Ions of valence greater than 4 reduce the oxygen vacancy concentration and the rate of anatase to rutile transformation. Similarly, substitution of two fluoride ions for an oxygen ion would reduce the number of anion vacancies and inhibit the transformation⁴⁴. Anatase to rutile transformation is also known to be greatly inhibited in the presence of SiO_2 ⁴⁵.

The morphology of the starting frustules had not been altered during the heat treatment (Figure 21). EDS spectrum also supports the XRD results. The large F peak observed before heat treatment is all but disappeared indicating the final composition of the

frustules was primarily Ti and O consistent with the XRD data showing a phase pure TiO_2 formation.

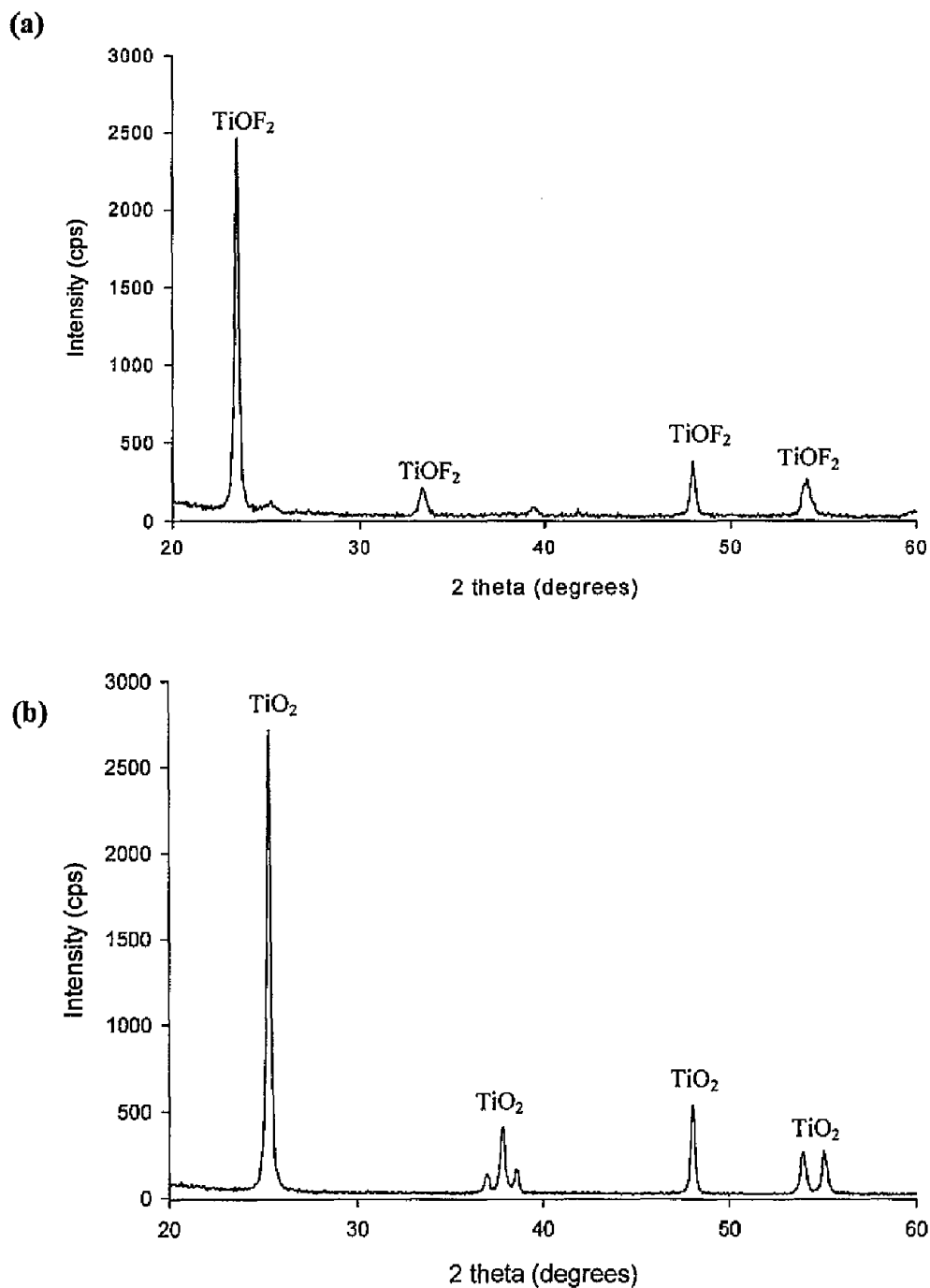


Figure 20: XRD pattern of frustules reacted with TiF_4 (a) shows that they are converted into TiOF_2 . (b) After heat treatment in air at 600 °C for 3 hours, anatase frustules formed.

The data presented was obtained by reacting as received frustules at 330 °C for 1 hour with 2.5 TiF₄ to SiO₂ molar ratio. Preliminary experiments for this system were carried out using a 1.2 TiF₄ to SiO₂ molar ratio. XRD pattern of these frustules revealed that TiO₂ was formed but the SEM micrographs showed that the frustules no longer retained their shapes. Additional experiments were conducted using different experimental parameters such as time, molar ratio of the reactants and total mass of the reactants in the reaction cell. The reactions carried out at 330 °C for 6 hours with a molar ratio of TiF₄ to SiO₂ higher than 3 resulted in retention of shape with TiOF₂ formation. They were converted into anatase by further heat treatments at 900 °C for 2 hours. The SEM micrographs display that the frustules were more porous and granular. Then, the experiments were carried out under milder conditions. Lower dwell time was set, and the heat treatment temperature was varied between 300 and 600 °C. Reheating at 300 °C for 2 hours did not completely convert the frustules into TiO₂. Conversion at 500 °C revealed anatase phase in the XRD patterns but EDS spectra still indicated the existence of fluorine. Heat treatments at 600 °C converted the frustules into titania and fluorine could no longer be detected with EDS.

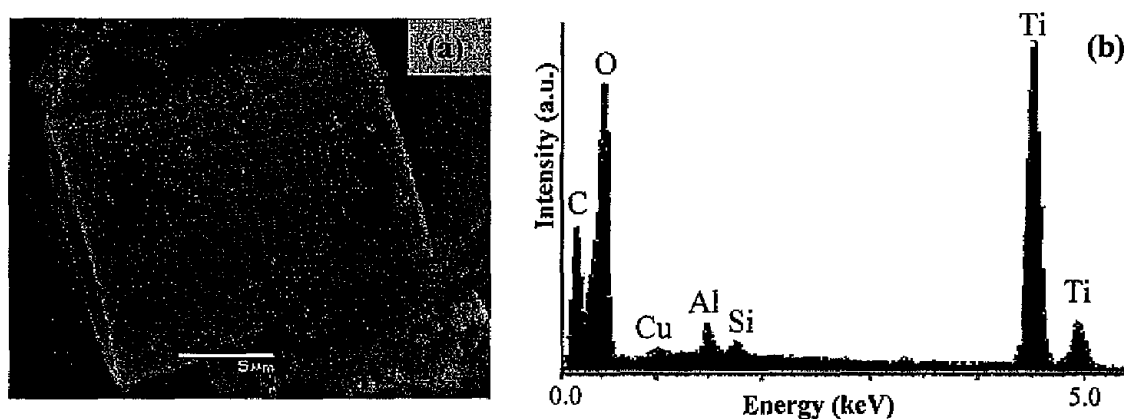


Figure 21: SEM micrograph of reacted frustule after heat treatment at 600 °C for 3 hours. EDS spectrum shows Ti and O peaks.

The chemical analysis result of the reacted frustules indicated that they include 90.7% TiO₂, 3.36% TiOF₂, 3.54% Al₂O₃, 1.1% Fe₂O₃, 1.32% CaO, 0.23% Na₂O, 0.22% MgO and 0.23% K₂O. Silicon content of the frustules was less than 0.1%. The calculations

showed that 100% of the frustules converted into TiOF_2 at 330 °C in 1 hour. 98% of the TiOF_2 frustules were converted into the TiO_2 with the heat treatment at 600 °C for 3 hours.

Crystallite sizes of the reacted frustules were calculated using the (101) diffraction line of anatase from the Scherrer formula. The crystallite size was calculated as 44.8 ± 3.4 nm for the samples reacted at 330 °C for 1 hour with 2.5 molar ratio of titanium tetra fluoride to silica. The crystallite size value determined with TEM micrographs coincide well with crystallite size calculated from XRD data. It is determined as 37 ± 13 nm. The SAD of reacted frustules indicates the anatase ring pattern (Figure 22).

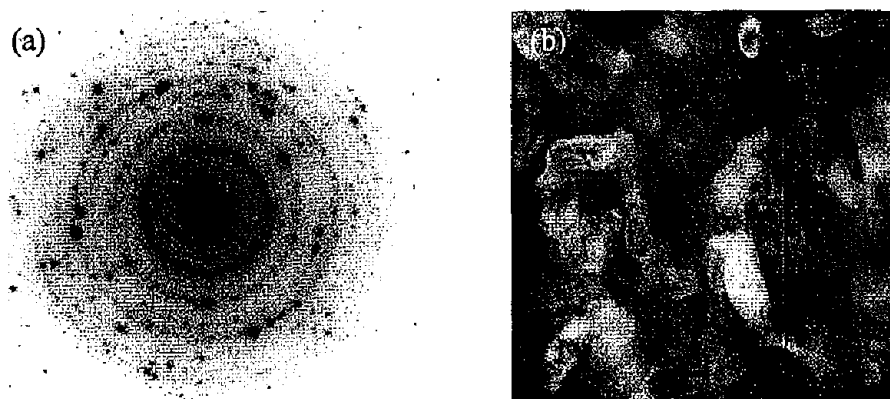


Figure 22: TEM micrographs verified that the crystal structure was anatase and the crystallite size was measured as 37 nm. The scale bar indicates 50 nm.

After reaction specific surface area of the frustules was measured as $10 \text{ m}^2/\text{g}$. SEM micrographs of the same frustules before and after the reaction indicated that the frustules shrank due to the molar volume difference between the silica and titania (Figure 23). A decrease in the specific surface area also would be expected due to the molecular weight increase during conversion. It was also mentioned that the frustules are more granular (Figure 19c). This might cause the pores to be clogged and decrease the specific surface area of the reacted frustules.

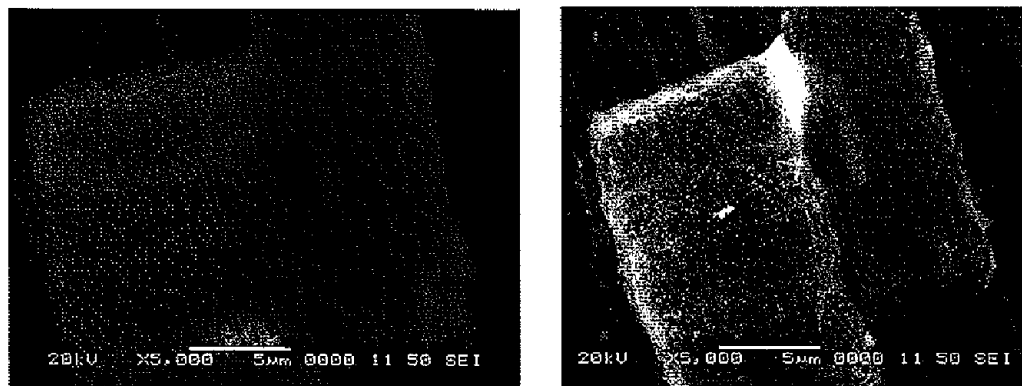


Figure 23: The SEM micrographs of the same frustules before and after the reaction at 330 °C for 6 hours.

4.2.2 Conversion to BaTiO₃

Preliminary experiments were carried out with reaction of TiO₂ (Titanium (IV) Oxide Anhydrous, 100%, Fisher Chemicals) powder and Ba(OH)₂·8H₂O at 95 °C for 4 hours. The XRD pattern revealed the formation of BaTiO₃ with residual TiO₂. Then the titania frustules reacted with Ba(OH)₂·8H₂O at 95 °C for 4 hours with a molar ratio (Ba(OH)₂·8H₂O/TiO₂) less than 1. SEM micrographs showed that the frustules did not retain their shapes. When the experiment was carried out at 100 °C for 3 hours with a molar ratio of 3, the XRD pattern indicated formation of BaTiO₃ and BaCO₃ with some residual TiO₂. Another experiment was run at 120°C for 3 hours with a molar ratio of 5 in a sealed reaction chamber which was loaded in the glovebox. Titania was no longer observed in the XRD pattern (Figure 23a). SEM micrographs showed that frustules retained their shapes (Figure 24b), but unreacted Ba(OH)₂ was also observed within the sample. When the heating rate was decreased from 10 °C/min to 0.4 °C/min, the frustules kept their shapes, and XRD pattern indicated existence of BaTiO₃ and TiO₂ with small amount of BaCO₃. Additional experiments must be conducted to eliminate residual Ba(OH)₂, and formation of BaCO₃, and it must be verified that the frustules were converted into BaTiO₃ completely.

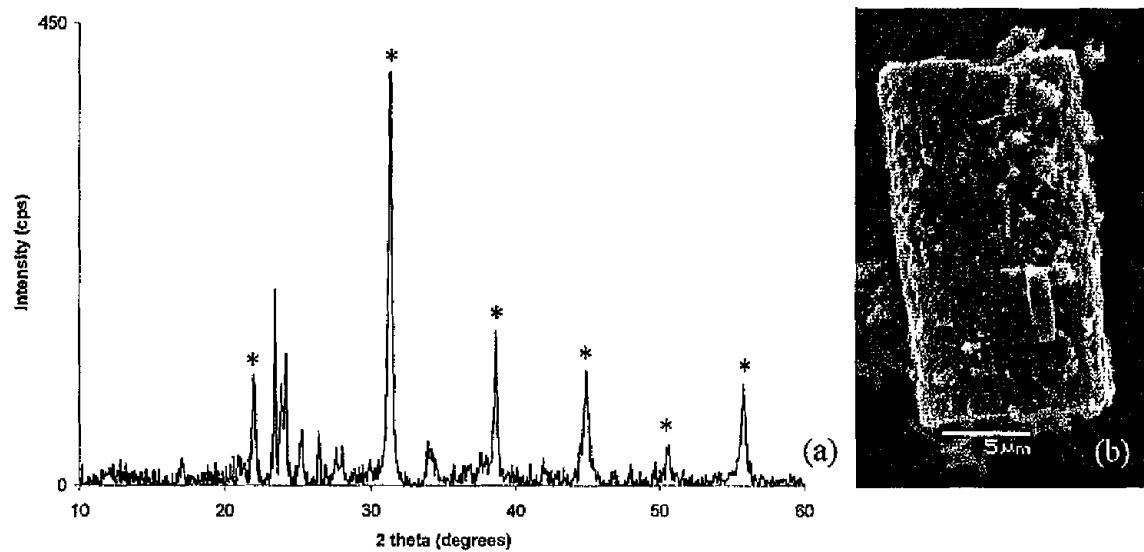


Figure 24: The SEM micrograph and XRD pattern of the frustules after the reaction. * indicates BaTiO_3 peaks. The other peaks belong to BaCO_3 .

5 SUMMARY AND FUTURE WORK

Conversion of microstructured silica diatoms to magnesium oxide and titanium oxide was demonstrated while maintaining the original overall shape and structure of the diatoms. Gas-solid displacement reactions were carried out in sealed reaction chambers with varying reactant ratios, total amount of reactants, temperature and time. The formation of magnesium oxide and titanium oxide and conservation of shape was confirmed by XRD, SEM, EDS, and TEM studies. The chemical composition of the reacted frustules was determined by wet chemical analysis.

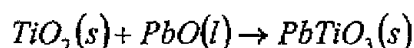
The frustules were converted to MgO through the reaction of SiO_2 frustules with gaseous Mg. The powder X-ray diffraction (XRD) pattern of natural and pyrolyzed frustules showed that they are mostly amorphous. XRD pattern of frustules after reaction revealed MgO peaks. SEM micrographs confirmed that the shape was retained. EDS also indicated the high intensity Mg peak. The completeness of the reaction was checked with the reaction between cristobalite and gaseous Mg. The XRD pattern did not include any cristobalite peaks at the end of the reaction at 900 °C for 4 hours. The wet chemical analyses results confirmed that the conversion was complete. Conversion percentage decreased with decreasing temperature due to the lower rate of the reaction. Temperature affected both the rate constant and vapor pressure of magnesium. It was observed that at lower temperatures and shorter reaction times conversion was incomplete with the intermediate compound Mg_2Si forming. Formation of Mg_2Si was also affected by the excess magnesium amount in the reaction cell. Crystallite size of the reacted frustules at 900 °C for 4 hours was calculated with the XRD data to be 27 nm. As expected it decreased with decreasing time and temperature. A decrease in the specific surface area of the frustules was observed after the reaction. TEM analyses verified the crystallite size measurements and crystal structure of the converted frustules.

Conversion of SiO_2 frustules to TiO_2 was studied by reacting the frustules with gaseous TiF_4 followed by heat treatment in air. Under the conditions investigated it appears that silica frustules react with TiF_4 to form TiOF_2 which is then converted to TiO_2 by heat treatment in air. SEM micrographs verified that the shapes of the frustules were preserved and XRD patterns showed that anatase polymorph of TiO_2 was formed. The crystal

structure of the reacted frustules was confirmed with the TEM data. Results of the chemical analysis indicated that the frustules no longer include silicon. The conversion reaction was completed at 330 °C in 1 hour. The crystallite size of the reacted frustules was calculated to be 45 nm. The specific surface area of the reacted frustules was determined as 9.5 m²/g.

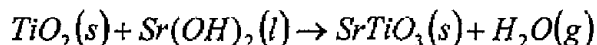
Following the conversion to titania reactions, an attempt made to convert TiO₂ into BaTiO₃. The preliminary conversion reactions were carried out with solid-liquid reaction of titania frustules with Ba(OH)₂. The experiments were run under different conditions, and it was observed that at 120°C for 3 hours the XRD pattern revealed BaTiO₃. SEM micrographs indicated preservation of the shape, however the sample contained debris from the solid-liquid reaction. Further experiments must be run to eliminate the debris, and a more thorough characterization is needed. As an alternative method, the conversion might be attempted with hydrothermal reactions. The synthesis of BaTiO₃ by the reaction of Ba(OH)₂ with TiO₂ in aqueous solution has been reported. Kuty *et al.*, and Pfaff⁴⁶ converted fine powders of TiO₂ into BaTiO₃ with suspending those particles in Ba(OH)₂ solution⁴⁷.

TiO₂ frustules can be converted into TiO₂'s functional derivatives such as BaTiO₃, PbTiO₃, and SrTiO₃. Conversion of silica to titania can be followed by conversion of titania to ATiO₃. The formation of BaTiO₃ has been attempted in this study, however further characterization is required. To form PbTiO₃ and SrTiO₃ following reactions might be used. For PbTiO₃:



Gibbs free energy of the reaction is -37.3 kJ/mol at 950 °C. The melting temperature of PbO is 888 °C, and the reaction would take place around 950 °C.

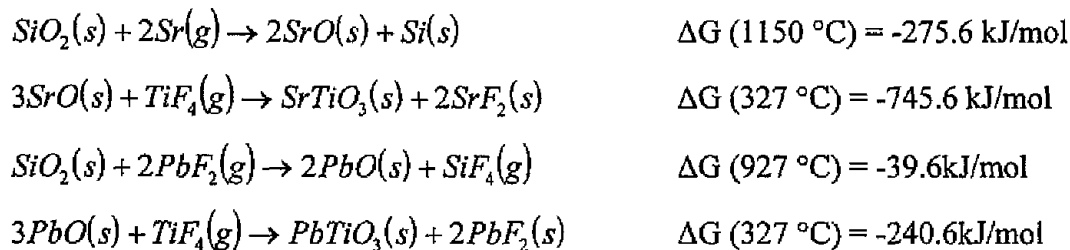
Conversion of frustules into SrTiO₃ reaction can be carried out using Sr(OH)₂.



This reaction is thermodynamically favorable with a Gibbs free energy of -101.5 kJ/mol at 600 °C. The experiment can be performed at 600 °C which is higher than the melting point of Sr(OH)₂ (Sr(OH)₂ melts at 510 °C).

As an alternative path for conversion, the conversion reaction may be started with silica frustules. Reaction with gaseous PbF₂ would form PbO, and reaction of vaporized Sr

with following reactions can be used. Melting temperatures of Sr, TiF_4 , and PbF_2 are 777, 284, and 818 °C respectively.

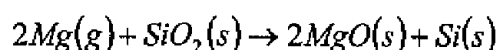


The present work has been focused on shape preserving displacement reactions and applications have been shown with the reactions of silica frustules and different compounds. Future genetic engineering could yield frustules with tailored, non-natural shapes and features for particular meso/nano device applications². Shape preserving displacement reactions could then be used to convert such shape-tailored preforms into nanostructured, micro devices as sensors, and self-repairing components in embedded structures with ability to respond to chemical, thermal, electronic, magnetic changes in the vicinity. Those devices may be used as reservoirs for indicator liquids, chemical sensors, micro-devices such as gears, switches, connectors, strain sensors, and microreactors with self-repair reactants⁴⁸.

APPENDIX

Calculation of the conversion percentage from the chemical analysis data for the frustules reacted with gaseous Mg at 800 °C for 4 hours is shown.

Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	Na ₂ O	MgO	Si	Total
2.79	0.94	0.91	0.19	0.51	62.2	24.34	91.88



According to the reaction every mole of silica produces 2 moles of magnesia and 1 mol of silicon. As it was mentioned before 92% of the unreacted frustules is silica. If we assume that x grams of silica reacts with gaseous magnesium, $\frac{80x}{60}$ grams of magnesium and $\frac{28x}{60}$ grams of silicon will be produced (molecular weights of SiO₂, MgO and Si are 60, 40 and 28 grams respectively.). After the reaction, there will be $(92 - x)$ grams of unreacted silica, produced magnesia and silicon and the other metal oxides in the frustules' side. The sum of these (A) would give us the total amount before normalization to 100, but since the chemical analysis result indicates Si percentage, Si coming from unreacted silica has to be calculated $(\frac{28(92 - x)}{60})$. We can calculate the value of x with magnesium balance and check the value of x with silicon balance.

$$\frac{(92 - x)28}{60} + \frac{28x}{60} + \frac{80x}{60} + 7.29 = A \quad (\text{total mass after reaction, before normalizing to 100\%})$$

$$\text{Mg balance: } \frac{80x}{60} * \frac{91.88}{62.2} = A$$

$$x = 78.47 \text{ and } A = 154.55$$

$$\text{Si balance: } \left[(92 - 78.47) * \frac{28}{60} + 78.47 * \frac{28}{60} \right] * \frac{91.88}{154.55} = 25.52$$

Analysis result: 24.34

The value of x was calculated out of 92. The percentage of the conversion is;

$$78.47 * \frac{100}{92} = 85.29\%$$

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