



Biologically-Derived Photonic Materials for Thermal Protection Systems

Sylvia M. Johnson, Thomas H. Squire, John W. Lawson

NASA Ames Research Center

Michael Gusman, ERC Corporation

K-H Lau and Angel Sanjurjo, SRI International

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 - Fundamental Aeronautics Program (Hypersonics)
 - Early experimental concepts: layered structures
 - Modeling of photonic heatshields
 - International Agreement with ETH (Switzerland) (Lawson)
 - Center Innovation Fund
 - “Computational Design of Photonic, Reflecting TPS” (J. Lawson, 2010)
 - Biologically Inspired Radiation Reflecting Ablator (BIRRA) (S. Johnson, 2011)



Clarification

- The radiation discussed here is that occurring in the shock layer during reentry that results in large heat fluxes. The goal is to develop TPS that will attenuate this radiative heating efficiently and reliably.
- Astronauts are exposed to solar and cosmic radiation in space which has deleterious effects. It is desirable to minimize exposure times with fast transit times which imply fast reentries and thus increased radiative heating. Radiation reflecting TPS is not designed to protect astronauts from radiation occurring in space.



Outline

- Radiation during Reentry
- Photonic Approach to Radiation Reflecting Heatshields
 - Theoretical Validation of Concept
 - One fabrication approach: Biologically based reflector (BIRRA)



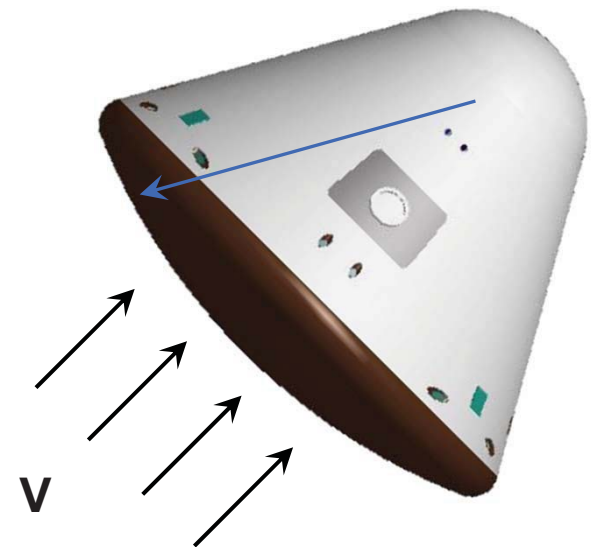
Reentry Heating Parameters

- Reentry heating comes from two primary sources
 - Convective heating from both the flow of hot gas past the surface of the vehicle and catalytic chemical recombination reactions at the surface
 - Radiation heating from the energetic shock layer in front of the vehicle
- Magnitude of stagnation heating is dependent on a variety of parameters, including reentry speed (V), vehicle effective radius (R), and atmospheric density (ρ)

$$\dot{q}_{conv} \propto V^3 \left(\frac{\rho}{R} \right)^{0.5}$$

$$\dot{q}_{rad} \propto V^8 \rho^{1.2} R^{0.5}$$

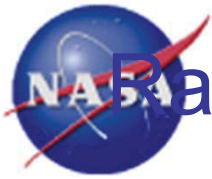
- As reentry speed increases, both convective and radiation heating increase
 - At high speeds, radiation heating can quickly dominate
- As the effective vehicle radius increases, convective heating decreases, but radiation heating increases



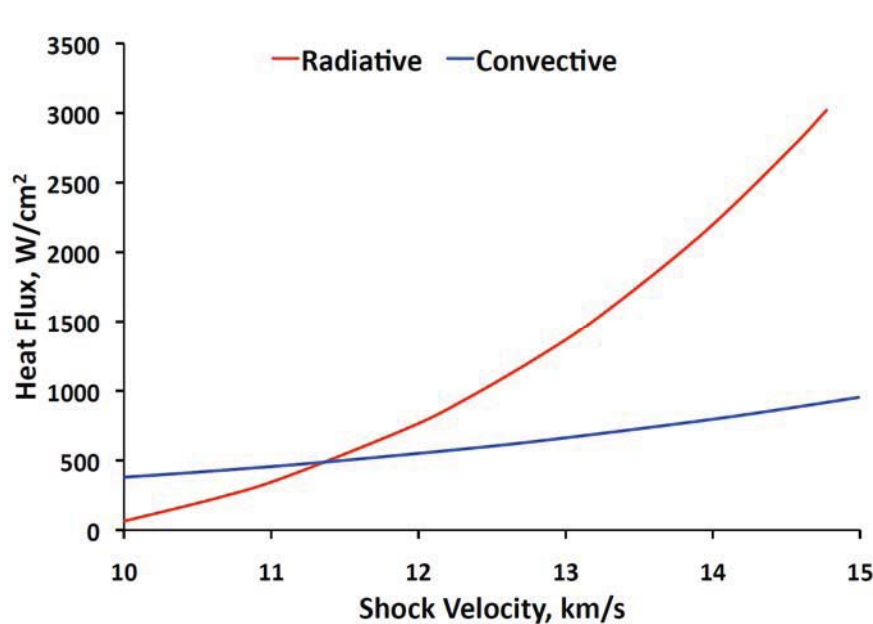


Radiation during Reentry

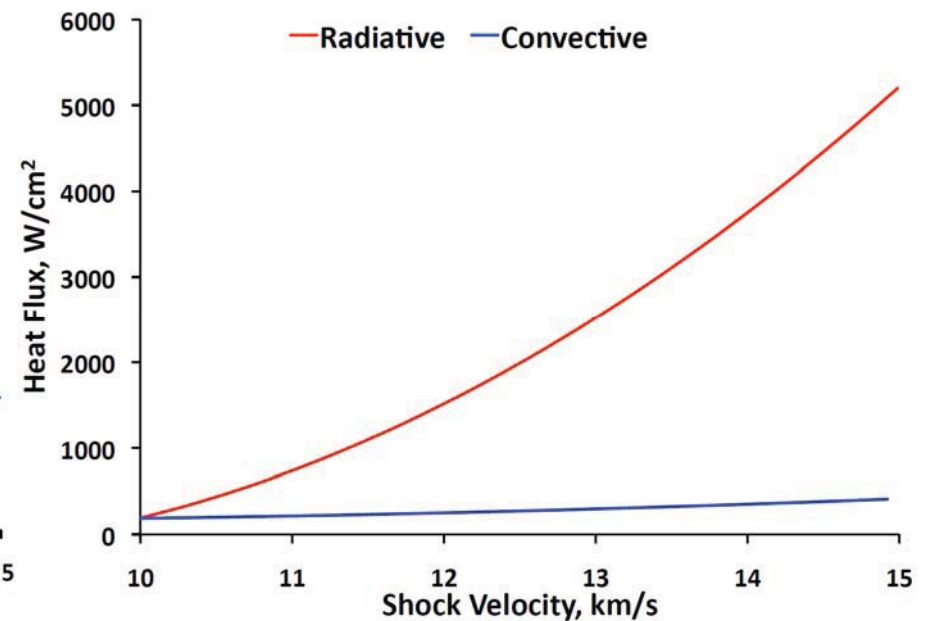
- Function of reentry speed:
proportional to V^8
- Occurs very early in reentry
- Occurs for very specific wavelengths
- Dependent upon atmosphere
composition



Radiation and Convection: Vehicle Size and Velocity (Earth)



1m radius sphere



5m radius sphere

- Relationship between radiative heating and nose radius is not linear (coupled radiation)
- Radiation dominates convection at ~11.5km/s for 1m radius
- Radiation dominates convection at ~10km/s for 5m radius

Figs from: Johnston et al. JSR 2013 and Brandis & Johnston 2014 AIAA (upcoming meeting)



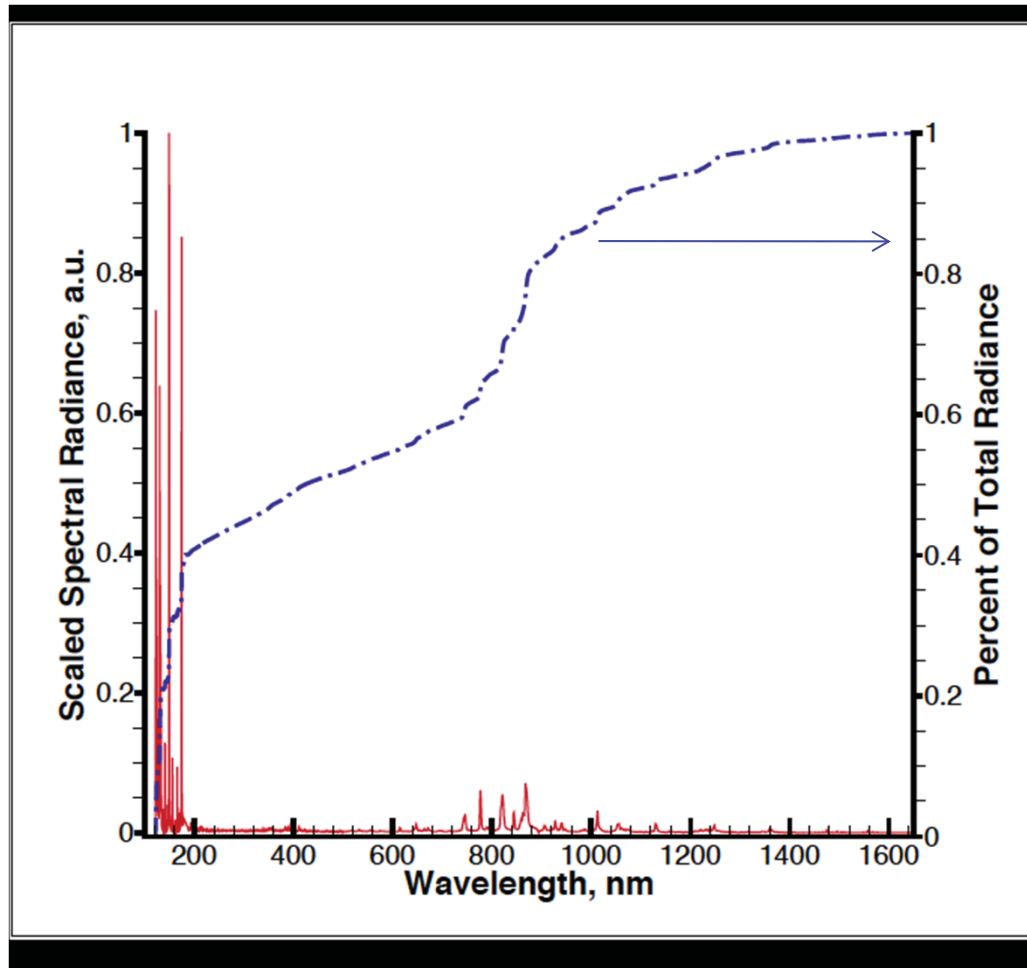
Heating Data for Various Planetary Entries

Peak Stagnation Point Conditions	Venus Mission			Saturn		Neptune/Uranus		Jupiter
	Direct	Aerocapture	From Orbit	Prograde	Retrograde	Direct	Aerocapture	Prograde
	B Coef (kg/m²)	193.0	114.0	114.0	256.0	256.0	260.0	498.0
V_e (km/s)	11.6	11.2	10.2	26.8	46.4	~29	~29	47.4
q_{conv} (W/cm²)	2,300	500	340	~3000	~15000	8,000	6600-7400	21,000
q_{rad} (W/cm²)	2,500	700	25	~0	~5000	4,000	3800-7400	40,000
q_{total} (W/cm²)	4,700	1,200	360	~3000	~20000	12,000	10400-14800	61,000
P_{stag} (atm)	10.0	0.3	0.3	1.4	10.0	<5	<1	9.5

Radiative heating is particularly significant for Jupiter prograde entry



Radiation Spectrum for Earth Entry

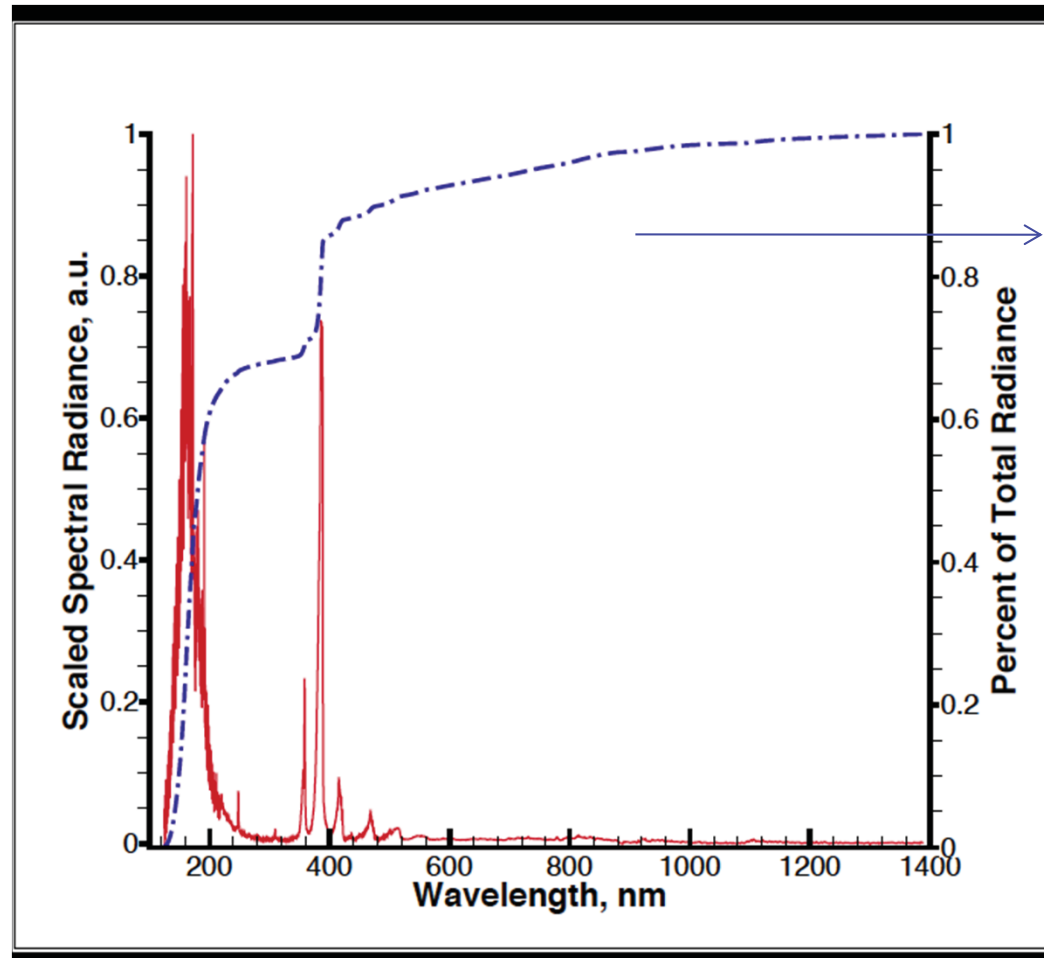


EAST data for Earth entry speed of 10km/s

Courtesy B. Cruden/A. Brandis/D. Prabhu



Radiation Spectrum for Mars Entry



EAST data for Mars entry speed of 6.5km/s



Where is Radiation-Reflecting TPS Beneficial?

- Entry into gas giants, especially at high latitudes has very large radiative heating component
 - Enable science missions
 - Need a TPS that is mass efficient to increase science payload
- Earth return from Mars with a crew will be a high speed entry
 - Reduce transit time for crew health
 - Need a TPS that can enable fast entry



Impact of Radiation Reflecting Heatshield on NASA Planetary Missions

- If we can reflect some part of the radiative heating then the overall heat load will be reduced.
- Reduction in heat load will mean less TPS mass is required, thus improving the payload mass (science payload) of a vehicle
- Reflecting concepts may be paired with carbon phenolic type of materials



Radiation Protecting TPS

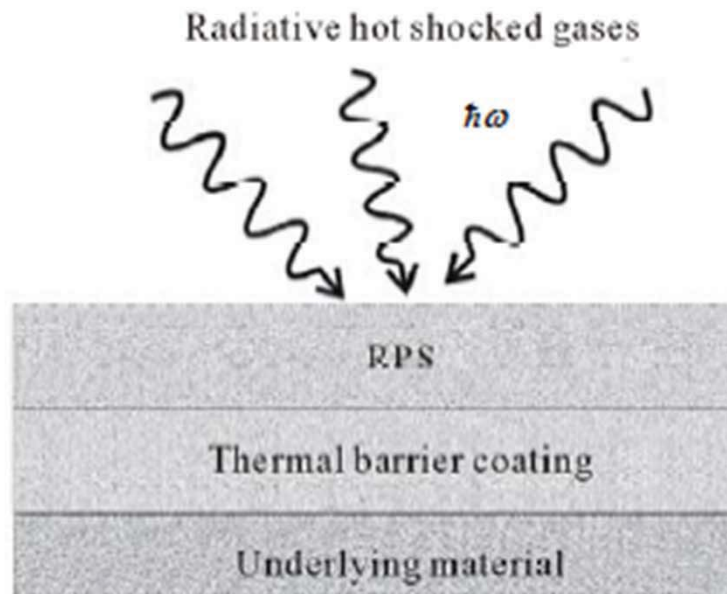


Figure 1. Schematic of a possible thermal protection system for a space vehicle. RPS protects against radiative heating. Thermal barrier coating retard conductive heat propagation.

- Radiation reflector is at surface
- Radiation reflection may require addition of an outer layer to existing materials such as carbon phenolic or derivatives

"Design of reflective, photonic heat shields for atmospheric reentry", N. Komarevskiy, V. Shklover, L. Braginsky, C. Hafner, O. Fabrichnaya, S. White and J. Lawson, J. Electromagnetic Analysis and Applications 3, (2011), p228

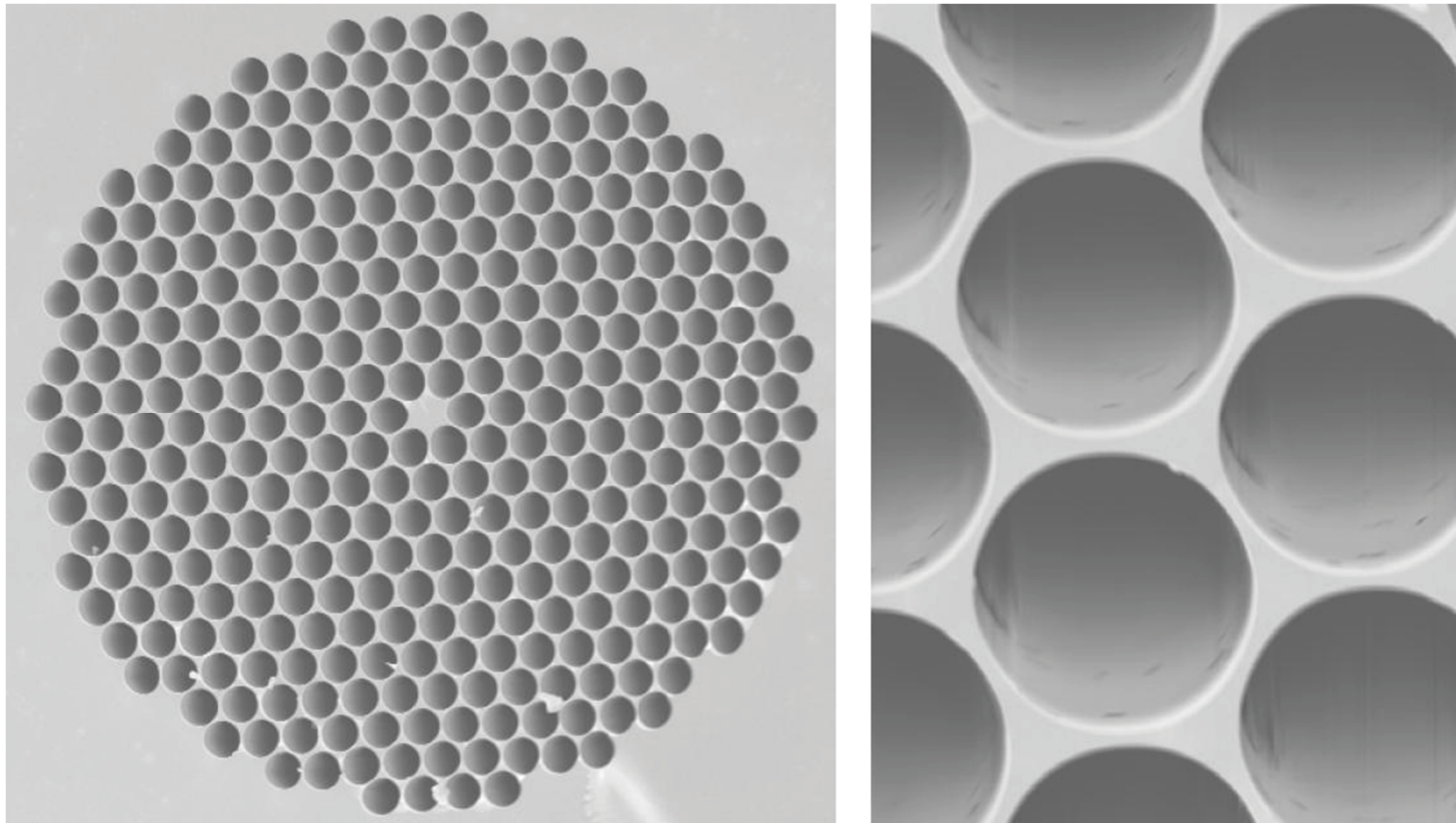


Photonics Background

- Tunable reflectors (for different planetary environments) can be constructed based on photonic structures
 - periodic arrangements of materials with contrasting dielectric properties.
 - internal reflections interfere destructively, blocking propagation of radiation into the material.
 - periodicity must be on the order of the wavelength to be reflected, which for EDL applications could be hundreds of nanometers.
- Fabrication of such small structures is very expensive and difficult but possible.



Photonic Crystal Fiber: Regular Array of Holes



SEM micrographs of a photonic-crystal fiber produced at US Naval Research Lab.
Hole diameter is $4\mu\text{m}$
Source: Wikipedia, http://en.wikipedia.org/wiki/Photonic_crystal_fiber



Computational Design of Photonic TPS

- Computational design (J. Lawson and coworkers) of photonic structures to reflect wavelengths relevant for Earth entry shock layer radiation

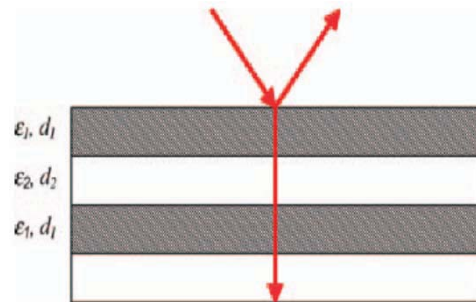
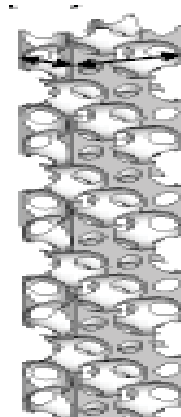
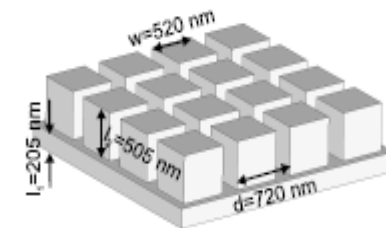


Fig. 5. Normal propagation of light through an infinite one dimensional "sandwich" $(\epsilon_1, d_1), (\epsilon_2, d_2), (\epsilon_1, d_1), (\epsilon_2, d_2), \dots$

Multilayers



Porous structures



Guided Mode Resonance

- References:

- *Potential of glassy carbon and silicon carbide photonic structures as radiation shields for atmospheric re-entry*, N. Komarevskiy, V. Shklover, L. Braginsky, C. Hafner and J.W. Lawson, Optical Express, (2012)
- *Fast numerical methods for the design of layered photonic structures with rough interfaces*, N. Komarevskiy, L. Braginsky, V. Shklover, C. Hafner and J.W. Lawson, Optical Express 19, (2011), p 5489
- *Design of reflective, photonic heat shields for atmospheric reentry*, N. Komarevskiy, V. Shklover, L. Braginsky, C. Hafner, O. Fabrichnaya, S. White and J. Lawson, J. Electromagnetic Analysis and Applications 3, (2011), p 228

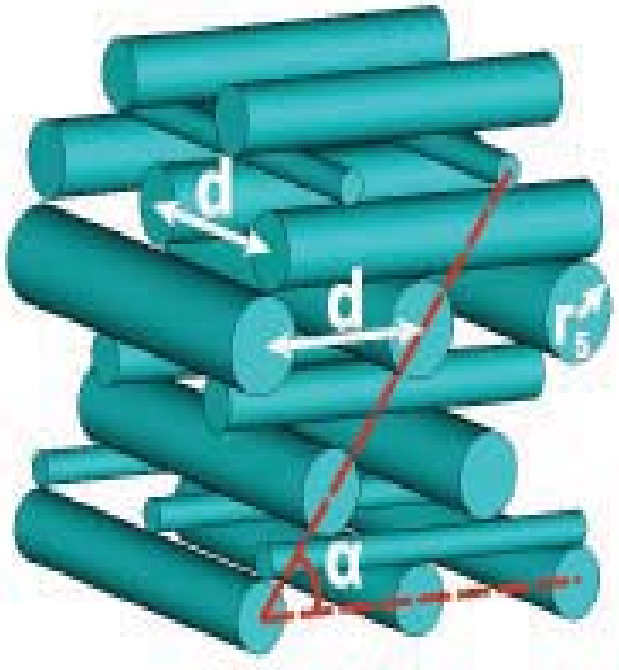


Fabrication Challenges

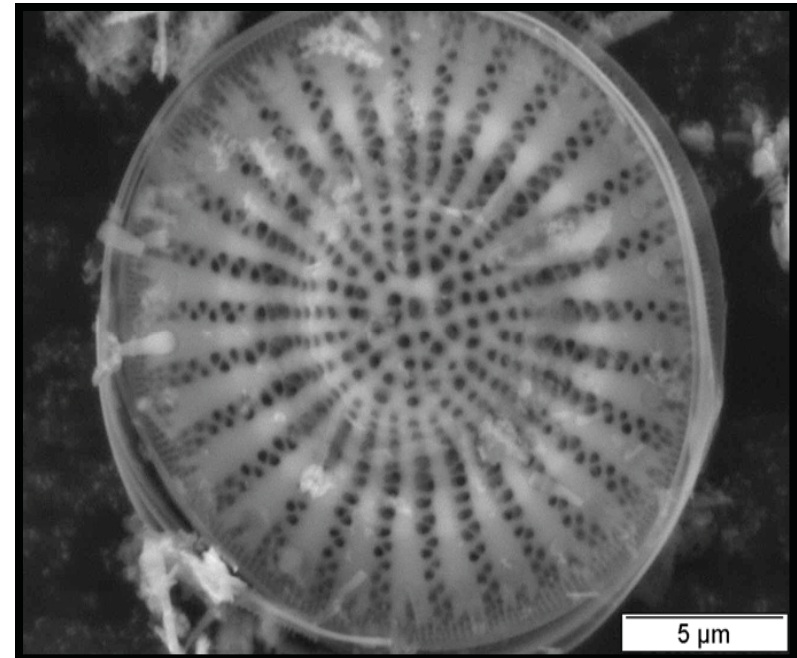
- Photonic or ordered structures can be made by various deposition and growth techniques. Photonic structures have been fabricated and are in use for a variety of applications
- Fabrication can be tedious or expensive and scale-up is an issue, especially for a TPS application
- Nature has created a wide variety of such structures in diatoms that contain periodic arrangements of materials in the desired size range.
- Diatoms generally range in size from $\sim 2\text{-}200\mu\text{m}$. The siliceous wall can be highly patterned with a variety of pores, ribs, minute spines, marginal ridges and elevations. The order in these structures is the key to their potential applicability.



Fabricated vs Biological Structures



8-layered wood pile structure obtained by modeling: “d” dimension is of the order of hundreds of nms, r dimension~10s of nm



Characteristic feature of diatoms is the biomineralized cell wall (frustule) consisting of amorphous silica



BIRRA Approach to Making a Photonic Heat shield

- BIRRA approach
 - Photonic structures are difficult and expensive to fabricate and scale-up
 - Nature makes periodic structures
 - Can we use natural structures but make them refractory and incorporate them into a TPS, especially at the surface?
 - Can we find natural structures which reflect the desired wavelengths?



Can we find natural structures which reflect the desired wavelengths?



Array: 1.78 x 2.30 mm

Trends in Biotechnology,
Vol.27, No.2



Diatoms as Photonic Crystals

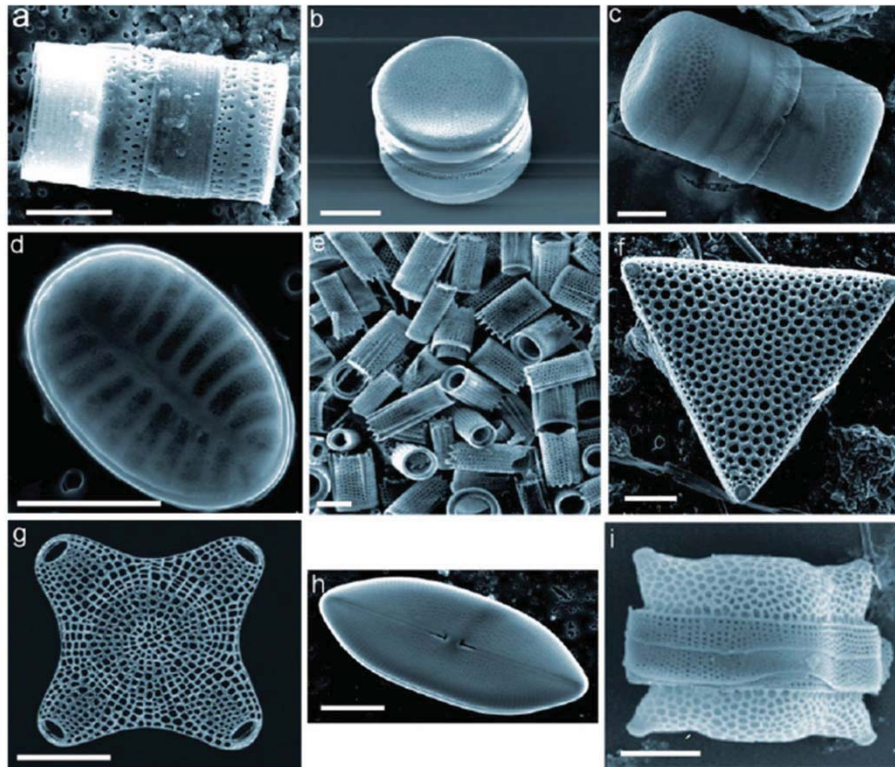


Figure 1. Extraordinary diversity of shapes and structures in diatoms. a–d) and f–i) SEM images of several marine diatom species. e) SEM of fossilized diatom biosilica structures from diatomaceous earth (Diatomite mine NSW, Australia) Scale bars: 10 μm

Adv. Mater. 2009, 21, 2947–2958

- Diatoms have photonic crystal properties—T. Furhrmann, et al., *Appl.Phys. B* 78, 257-260 (2004)
- The diatom cell forms regular arrays of chambers and pores in the cell wall, allowing only certain wavelengths of light to pass through
- A diatom cell can be regarded as a ‘photonic box’ with walls of photonic crystals

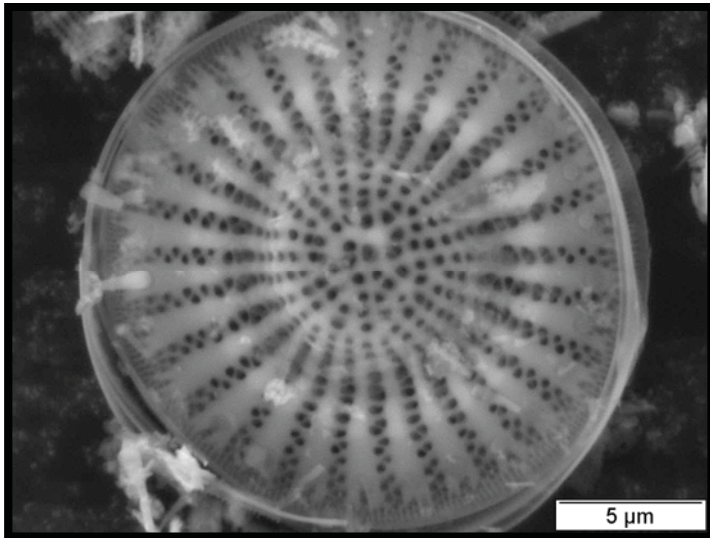


BIRRA Approach

- Convert amorphous silica of diatom to a more refractory material—SiC
- Measure reflectivity
- Incorporate into a TPS, especially near the surface
- Different species should reflect different wavelengths
- Progress :
 - Have demonstrated partial conversion to SiC and intermediates
 - Retain structure but somewhat coarsened



Diatoms: Starting Material Mined from Natural Deposits



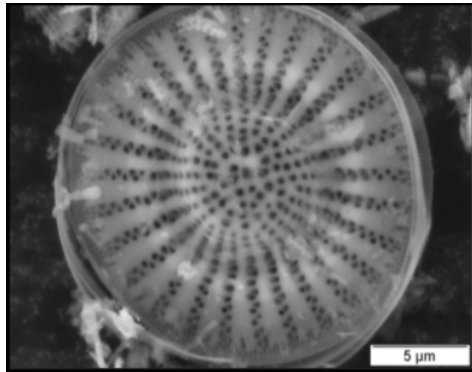
As-Received Diatom
Round pores~ 250nm average diameter

Characteristic feature of diatoms is the biomineralized cell wall (frustule) consisting of amorphous silica. Each cell consists of two halves, the thecae, which can be divided into a valve and one or more girdle bands

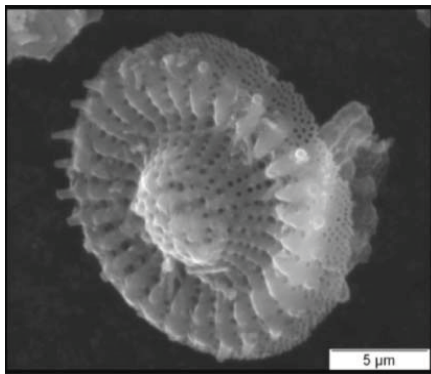
- Skeleton of a single celled algae formed in fresh and salt water
- 10s of 1000s of species with different structures
- Diatoms have been shown to have photonic effects
- Features are submicron
- Cell wall is amorphous silica
- Structure is on various levels
- Starting material consists of intact and many broken pieces



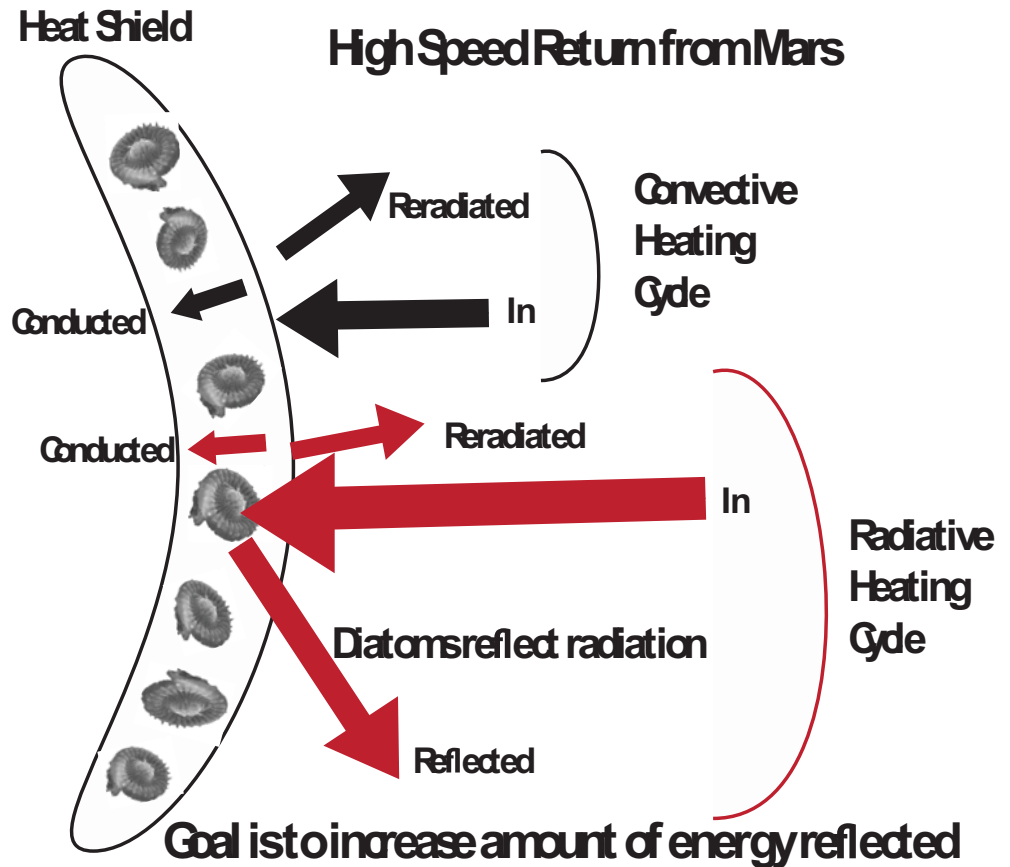
Incorporation of Converted Diatoms into Heat Shield



Cleaned Diatom



Diatom partially converted to SC

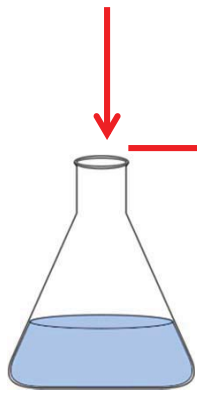




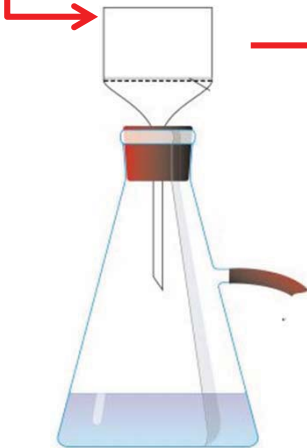
Converting Diatomite SiO_2 to SiC



Extraction sample



Wash

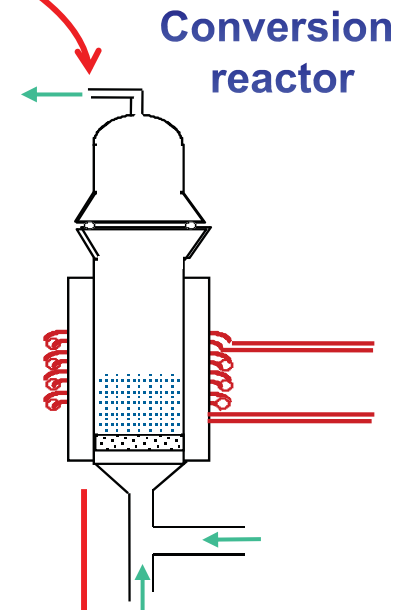


Filtration

Characterization
SEM, XRF, BET



Oven Dry

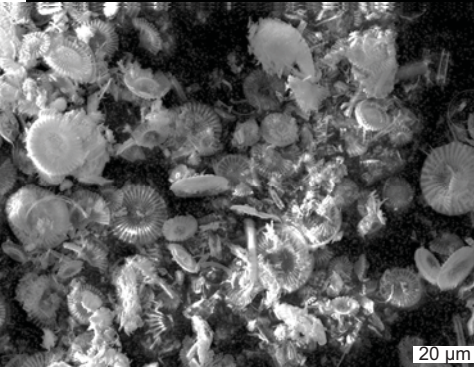
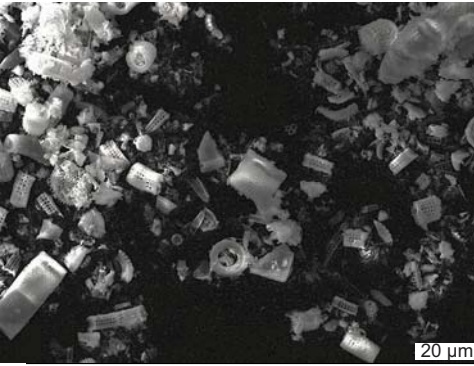


Conversion reactor

Characterization
SEM, XRF, Reflectan



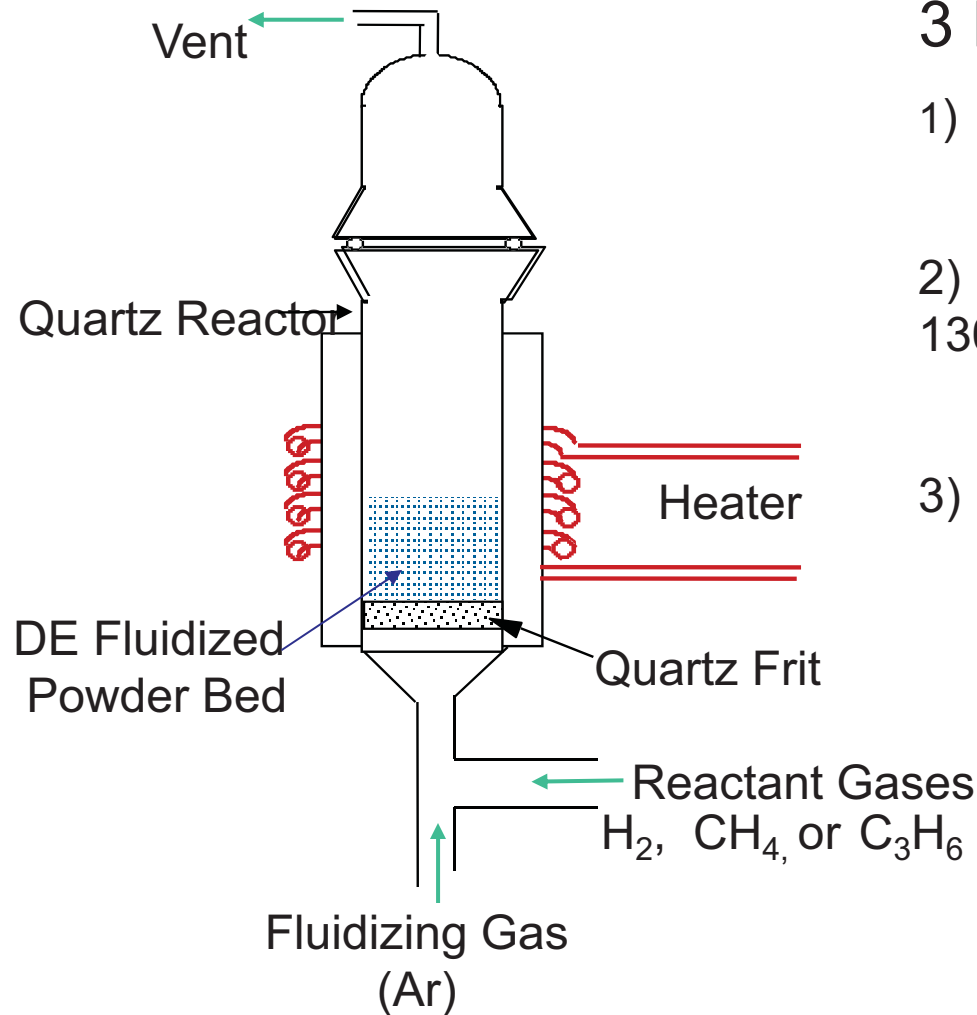
XRF of Extraction Samples: As-Received and Washed

Extraction Sample	Al	Si	Ca	Ti	Mn	Fe	Sr	Zr	Pb	
	No.1 As Received	1.6	89.6	3.2	0.6	0.06	4.9	0.02	-	-
	No.1 Washed	0.9	97.3	0.6	0.5	-	0.7	-	-	-
	No.2 As Received	2.8	84.5	3.2	1.4	0.05	7.9	0.04	0.03	0.03
	No. 2 Washed	1.4	94.0	0.7	1.7	-	2.2	-	-	-

Sample 1: Larger size easier to fluidize and lower iron content to interfere with conversion reactions

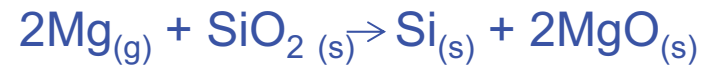


Fluidized-Bed Reactor (FBR) Conversion Method



3 Reactions in Process

- 1) In FBR at low temperature $\sim 600^\circ\text{C}$



- 2) In FBR at high temperature $\sim 800^\circ - 1300^\circ\text{C}$

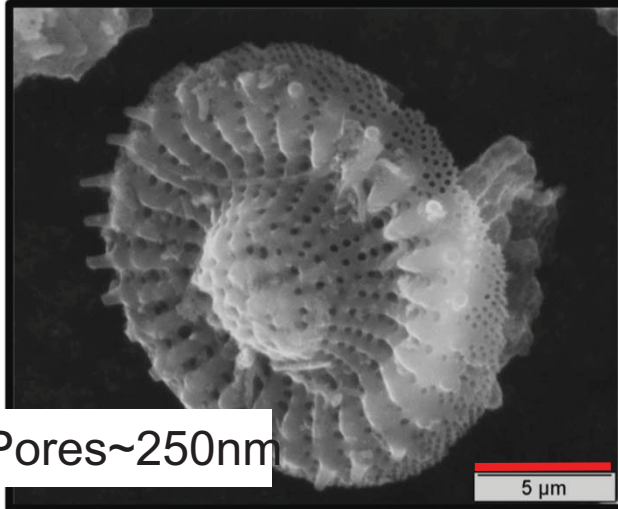


- 3) Leach to wash out Mg





Processing in FBR vs. Steel Ampoule Better Retention of Pores



Pores~250nm

5 μm

Fluidized Bed Reactor
Processing

Conversion at:

640°C for 5 h

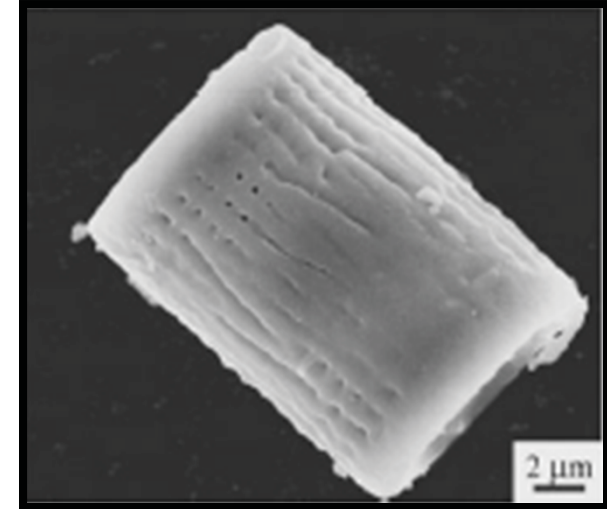
plus

850°C for 1.5 h

Then dissolution of MgO in
HCl

Steel Ampule
Processing
Magnesiothermic
reduction at:

650°C for 2.5 h

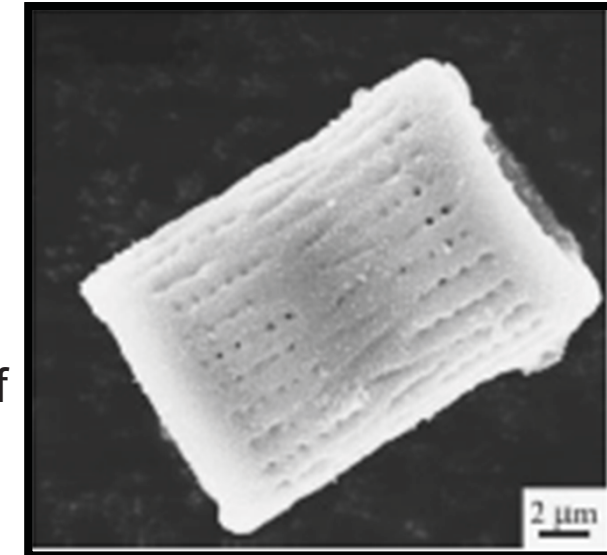


2 μm

5 μm

900°C for 1.5 h

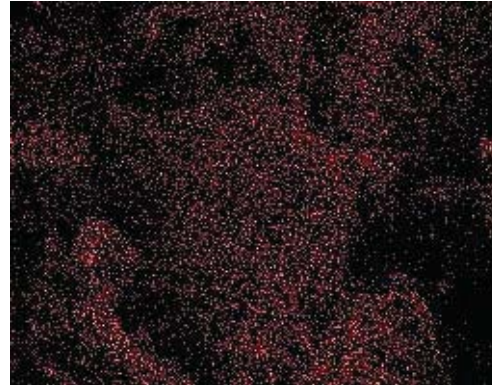
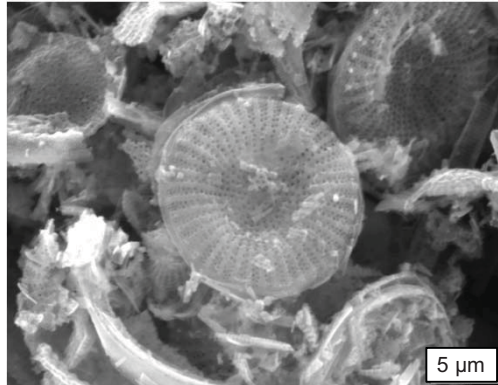
Then dissolution of
MgO in HCl



2 μm



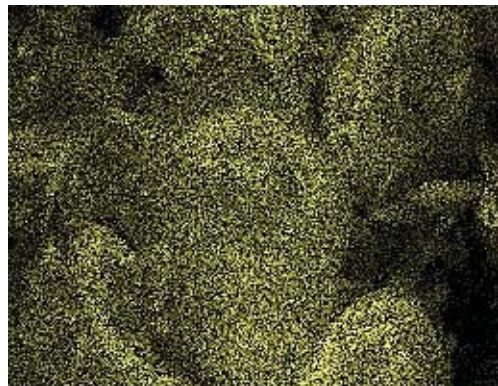
Element Mapping after 840°C in Ar/Ch₄/H₂



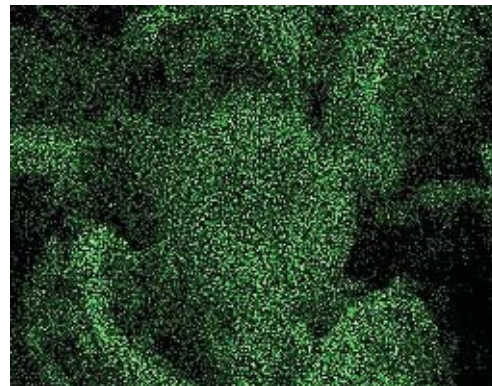
Carbon is present on frustule; amorphous carbon not detectable in XRD

CK (carbon)

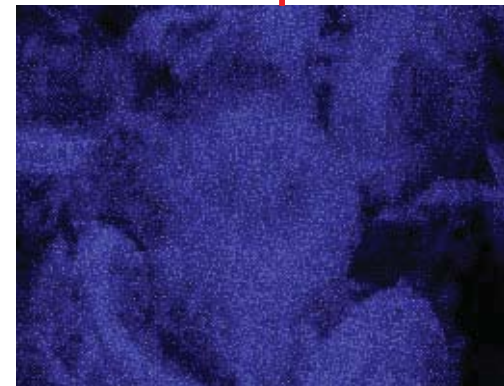
Mg presence before leaching process



SiK (silicon)



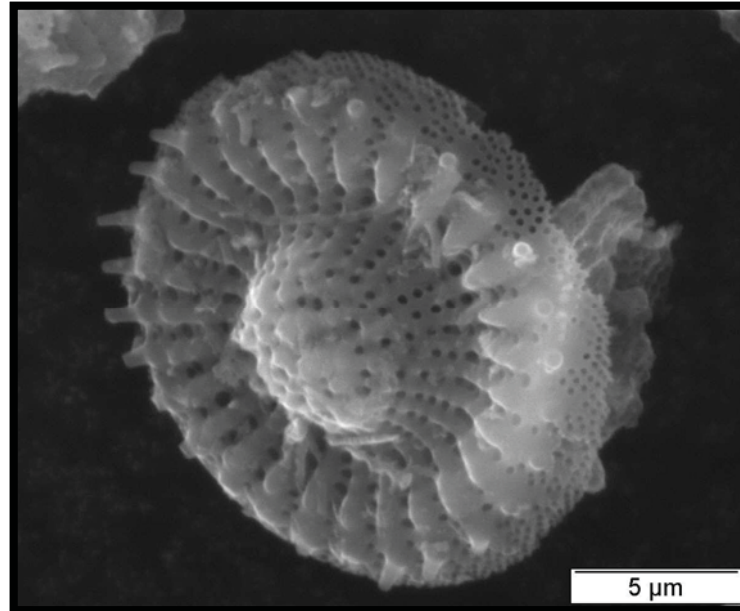
OK (oxygen)



MgK (magnesium)



Partially Converted Diatom



Some coarsening of microstructure but periodic arrangement of nanometer pores is still evident after conversion to silicon



Summary

- Have investigated an approach to using naturally occurring structures to make ordered high temperature materials
- Protection from radiative heating will be critical for future missions such as probes to Jupiter or high speed crewed entries to Earth and Mars.
- Photonic effects can be used to reflect radiation
- Photonic structures can be computationally designed and synthetically fabricated
- Natural structures may offer a way to make ordered structures efficiently
- Diatoms are an example
- Current effort is TRL-1-2.



Further Work

- **BIRRA (biologically –based photonic structures)**
 - Refine and optimize conversion process
 - Develop techniques for evaluating reflectivity
 - Survey available diatoms for structures of the appropriate size (changes on conversion)
 - Investigate potential of other natural structures
- **Synthetic approaches to photonic structures**
 - Take advantage of new approaches to making photonic structures by synthetic processes cheaper
- **Fabrication of photonic thermal protection system**
 - Common to biological or synthetic source of photonic components
 - Incorporate photonic structures into a TPS, especially at the surface
 - Evaluate performance of TPS in radiative /convective heating



Backup



Early Work on Reflecting TPS

- Fused Silica Reflecting Heat Shields for Outer Planetary Entry Probes, W.M. Congdon and D.L. Peterson, AIAA 10th Thermophysics Conference, 1975
- Used porous fused silica of various controlled particle sizes (monodisperse , binary and continuous particle size mixtures)
- Particle sizes: 2~3 μm , also colloidal silica (<1 μm)
- With and without additives.
- Some crystallization depending upon heat treatment (quartz, cristobalite)
- Tested in Ames Advanced Entry Heating Simulator (AEHS)
 - Convective heating: ~1.2kW/cm²
 - Radiative heating :0.5 to 3.0 kW/cm²
 - Few seconds (1~3)
- Surface melting
- “Higher reflectance and lower transmittance when compared to continuous silica of the same material”
- Smaller voids produced greater reflectance
- Very high reflectance~>0.8 μm



References

- **Technical Evaluation of the NASA Model for Cancer Risk to Astronauts Due to Space Radiation, NRC Report, 2012**
- **Fused Silica Reflecting Heat Shields for Outer Planetary Entry Probes, W.M. Congdon and D.L. Peterson, AIAA 10th Thermophysics Conference, 1975**
- **"Potential of glassy carbon and silicon carbide photonic structures as radiation shields for atmospheric re-entry", N. Komarevskiy, V. Shklover, L. Braginsky, C. Hafner and J.W. Lawson, Optical Express, (2012)**
- **"Fast numerical methods for the design of layered photonic structures with rough interfaces", N. Komarevskiy, L. Braginsky, V. Shklover, C. Hafner and J.W. Lawson, Optical Express 19, (2011), p 5489**
- **"Design of reflective, photonic heat shields for atmospheric reentry", N. Komarevskiy, V. Shklover, L. Braginsky, C. Hafner, O. Fabrichnaya, S. White and J. Lawson, J. Electromagnetic Analysis and Applications 3, (2011), p228**
- **A. Brandis, C. Johnston, B. Cruden, D. Prabhu, and D. Bose, "Uncertainty analysis of NEQAIR and HARA predictions of air radiation measurements obtained in the EAST facility," in 42nd AIAA Thermophysics Conference. American Institute of Aeronautics & Astronautics (AIAA), 2011.**
- **C.O. Johnston et al, " Assessment of Radiative Heating Uncertainty for Hyperbolic Earth Entry", in 42nd AIAA Thermophysics Conference. American Institute of Aeronautics & Astronautics (AIAA), 2011**
- **L. De Stefano et al, "Nano-biosilica from marine diatoms: A brand new material for photonic applications" Superlattices and microstructures 46 (2009) 84-89 (Elsevier)**
- **T. Fuhrmann, S. Landwehr, M. el Rharbi-Kucki, M. Sumper, "Diatoms as living photonic crystals" Appl. Phys. B 78, 257-260 (2004)**