

The selective dissolution of rice hull ash to form $[\text{OSiO}_{1.5}]_8[\text{R}_4\text{N}]_8$ ($\text{R} = \text{Me}$, $\text{CH}_2\text{CH}_2\text{OH}$) octasilicates. Basic nanobuilding blocks and possible models of intermediates formed during biosilicification processes†

M. Z. Asuncion,^b I. Hasegawa,^d J. W. Kampf^a and R. M. Laine^{*bc}

Received 14th February 2005, Accepted 11th March 2005

First published as an Advance Article on the web 22nd April 2005

DOI: 10.1039/b502178b

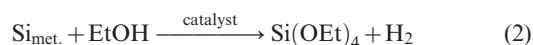
Rice hull ash (RHA) silica (80–98 wt.% amorphous, $>25 \text{ m}^2 \text{ g}^{-1}$ silica, 2–20% porous amorphous C) can be depolymerized in aqueous alcohol with $[\text{NR}_4]_8\text{OH}$ ($\text{R} = \text{Me}$, $\text{CH}_2\text{CH}_2\text{OH}$) under ambient conditions with the selective formation of octasilicate anions, $[\text{NR}_4]_8[\text{OSiO}_{1.5}]_8$. Dissolution kinetics were studied as a function of base and water concentration and temperature. Dissolution rates were determined by conversion of the octaanion to $[\text{HMe}_2\text{OSiO}_{1.5}]_8$, OHS. Activation energies for dissolution were $5 \pm 1 \text{ kcal mol}^{-1}$, much lower than for typical base-promoted silica dissolution. Furthermore, dissolution was not catalytic in base as found for other base-promoted silica dissolution reactions. Reaction rates were dependent on ammonium base and water concentrations and temperature. Dissolution was optimal at approximately one equivalent of $[\text{NR}_4]_8\text{OH}$ and three equivalents of water for choline hydroxide and five equivalents of water for $[\text{NMe}_4]_8\text{OH}$. A single crystal study of the octacholine $[\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}]_8$ derivative indicates that the compound crystallizes with three equivalents of water per $\text{SiO}_{1.5}$ suggesting that the rate limiting step in the dissolution process may be formation of the octaanion which is in accord with theoretical E_a 's calculated for the condensation of polyhydroxyl siloxanes. Octasilicate anions offer access to novel polyfunctional silsesquioxane platforms with each functional group occupying a single octant in Cartesian space. These platforms offer potential as precursors to dendrimers and hyperbranched polymers, and as nanobuilding blocks for the formation of nanocomposites. Furthermore, choline is structurally similar to: (1) ϵ -*N,N,N*-trimethyl- γ -hydroxy-lysine, (2) the oligomeric *N*-methylpropylamine components found in silafins, and (3) possibly the hydroxyamino acid units found in sponge filament proteins; all of which are thought to play a role in silica accretion, transport and deposition in diatoms and sponges. Thus, the octasilicate structure may reflect the structure(s) of species involved in silica transport and/or deposition in biosilicification processes.

Introduction

Worldwide production of rice hulls is estimated to be 80 M tons per year. Much of this is burned for its fuel value (electric power generation) creating >3 M tons per year of rice hull ash, RHA.¹ RHA consists of 80–98 wt.% amorphous silica with surface areas of up to $40 \text{ m}^2 \text{ g}^{-1}$ with the remainder being amorphous, porous carbon.^{2–4} RHA is produced in such quantities, with only limited commercial utility, that it is of growing environmental concern. Consequently, there is considerable interest in finding uses for RHA, especially as a source of silicon containing chemicals.

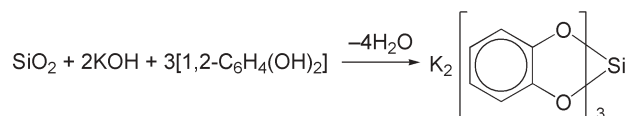
Currently most silicon compounds derive from Si metal, produced by carbothermal reduction of silica in a

high temperature, capital equipment and energy intensive process:⁵



(silicone/polysiloxane precursor)

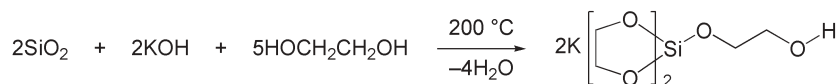
The possibility of producing silicon-containing chemicals directly from silica has been explored repeatedly over the years, beginning in the 1930's. Rosenheim *et al.* demonstrated



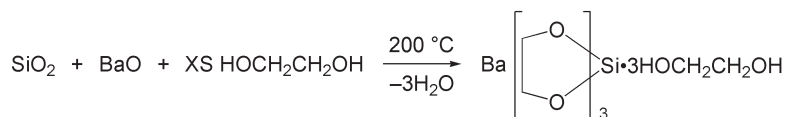
Scheme 1

† Electronic supplementary information (ESI) available: Crystal structure data in .CIF format. See <http://www.rsc.org/suppdata/jm/b5/b502178b/>

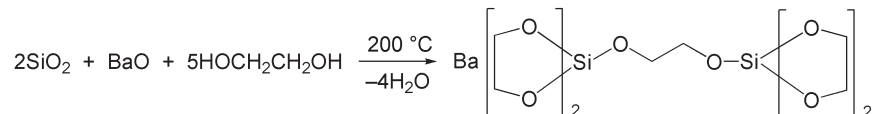
*talsdad@umich.edu



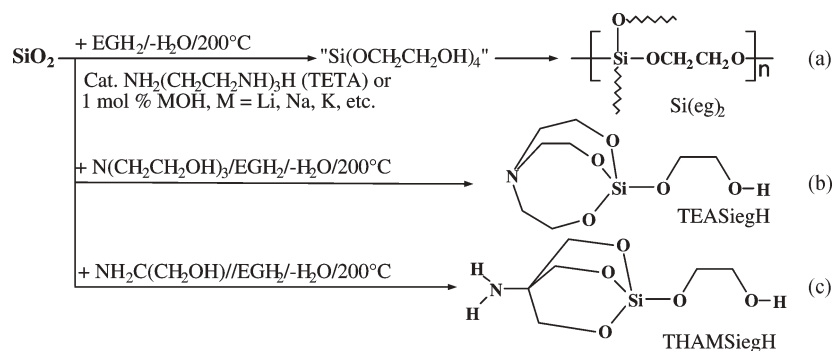
Scheme 2



Scheme 3



Scheme 4



Scheme 5

that alkali catecholates will depolymerize silica, sand and even quartz powder, Scheme 1.⁶ Work by Barnum,⁷ Weiss *et al.*,⁸ Frye,⁹ Boer and Flynn *et al.*,¹⁰ and Corriu *et al.*^{11,12} on this same reaction shows a recurring interest in SiO₂ depolymerization.

A patent by Bailey *et al.* describes heating silica in mixed solvents of alcohols (ethanol or propanol) and aromatic hydrocarbons (benzene or xylene) with 0.1 equiv. KOH (CsOH) for 16 h (120 h) at 200 °C (120 °C) to give 50–80% conversion to the corresponding alkoxy silanes.¹³ In related work, Goodwin and Kenny report¹⁴ that acidification of silicate anions in a toluene–ethanol azeotrope provides modest to good yields of tetraalkoxy silanes.

Suzuki *et al.* find that gaseous dimethyl and diethyl carbonate react with alkali-treated silica at 225° to 325 °C to form the respective alkoxy silanes quantitatively.¹⁵ This latter work has been followed up by extensive efforts by Lewis *et al.* demonstrating that a number of silica sources can be used and that, in some instances, methylsilanes can also be produced.¹⁶

We have also explored silica dissolution using the saturated analog of catechol, ethylene glycol (egH₂), giving quantitative yields of new glycolatosilicates,^{17–20} Schemes 2–4, and alkoxy silanes as illustrated in Scheme 5 (a–c).

SiO₂ dissolution in Scheme 2 [fused SiO₂ (8 m² g⁻¹)] is first order in base, [KOCH₂CH₂OH] and surface area. *E_a* for SiO₂

dissolution is 14 kcal mol⁻¹, Δ*H*[‡] = 11 kcal mol⁻¹, Δ*S*[‡] = –44 cal mol⁻¹ K⁻¹. The slow step is loss of H₂O from the SiO₂ surface.¹⁹ Dissolution thermodynamics are similar to those found for pressurized SiO₂ dissolution in aqueous base at similar temperatures, used commercially to make silicates.^{21,22}

For Scheme 5(a–c), where the products are neutral alkoxy silanes, the activation energies are similar,¹⁹ but the reaction rates with amine base catalysts are much slower because of their lower basicities as suggested by their p*K_b*s, Fig. 1. The search for stronger, non-alkali bases for the above reactions led to Me₄NOH and [Me₃NCH₂CH₂OH]OH.

The literature on the reactions of Me₄NOH with Si(OEt)₄ (TEOS),^{23,24} suggested the work reported here wherein we describe the use of [NR₄]OH (R = Me, CH₂CH₂OH) to depolymerize the silica of a common RHA under very

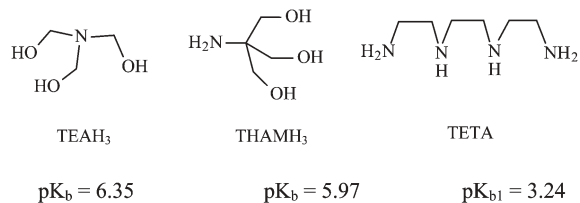


Fig. 1 p*K_b*s of selected tertiary amines used to catalyze silica dissolution.¹⁹

mild conditions to form the octasilicates, $[\text{NR}_4]_8[\text{OSiO}_{1.5}]_8$, exclusively.

Experimental

Analytical methods

^{29}Si Nuclear magnetic resonance (NMR) studies were carried out on a Bruker 360 MHz spectrometer using 11° pulse widths and a scanning width of 20 000 Hz. The FID signals were treated with a LB value of 5. Samples (200–500 mg estimated by TGA data) in 10–15 ml EGH_2 were placed in 10 mm NMR tubes with an inner 5 mm NMR tube containing acetone- d_6 as lock solvent and tetramethylsilane (TMS) as an external given reference. Samples were scanned 1000–4000 times.

Thermal gravimetric analysis (TGA) was conducted using a TA Instruments 2950 Thermal Analysis Instrument. Samples (30–60) mg were loaded in platinum pans and heated under N_2 balance (40 cc min^{-1}) with an air purge (60 cc min^{-1}), using a high-resolution (Hi-Res 4) program with a maximum ramp rate of $50 \text{ }^\circ\text{C min}^{-1}$ to temperatures of $950 \text{ }^\circ\text{C}$. The rice hull ash received as a gift from Uncle Ben's[™] was determined by TGA to contain 94.7 wt.% silica and 5.3 wt.% carbon.

Surface area analyses: specific surface areas (SSAs) and micropore analyses were conducted at 77 K using a Micromeritics ASAP 2000 sorption analyzer (Norcross, GA) with N_2 as the adsorbate gas. Samples were degassed at $110 \text{ }^\circ\text{C}$ for 4 h, then at $400 \text{ }^\circ\text{C}$ until the outgas rate was $<5 \text{ mm Hg min}^{-1}$ (typically 4 h). SSAs were calculated using the BET multipoint method with at least five data points with relative pressures between 0.001 and 0.20. Micropore analyses were conducted using the density functional theory (DFT) and a model that uses a set of isotherms in which N_2 is adsorbed on a C substrate with slit-like pores. Analysis was done with a software package supplied with the instrument. The surface area of the rice hull ash was found to be $22 \text{ m}^2 \text{ g}^{-1}$.

Chemical analysis: Powders were submitted to the University of Michigan Department of Chemistry's analytical services group for elemental analysis of carbon, nitrogen, and hydrogen content (CHN). A Perkin-Elmer (Norwalk, CT) 2400 CHN Elemental Analyzer was operated at $1000 \text{ }^\circ\text{C}$ (combustion tube) and $640 \text{ }^\circ\text{C}$ (reduction tube) with He as the carrier gas. Powder samples (1.5–2.0 mg) were loaded into tin vials. Acetanilide was used as the reference standard, and was analyzed in the same fashion as the samples. Duplicate analyses were performed. The instrument's detection limit is 0.10%. The samples from were found to have 4.38% average carbon content and hydrogen and nitrogen contents less than 0.10%.

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 5DXB FT-IR 300 spectrometer. Random cuttings of crystalline, optical-grade KBr from International Crystal Laboratories were used to prepare samples. About 600 mg of KBr was ground in a mortar with a pestle, and enough solid sample was ground with KBr to make a 1 wt.% mixture for making KBr pellets. After the sample was loaded, the sample chamber was purged with nitrogen for a minimum of 10 min before data collection. A minimum of 32 scans was collected for each sample at a resolution of $\pm 4 \text{ cm}^{-1}$.

X-Ray diffraction analysis (XRD) was performed on a Rigaku Rotating Anode Goniometer (Rigaku Denki, LTD., Tokyo, Japan). The powder sample was packed on a glass specimen holder. XRD scans were made from 10° to $60^\circ 2\theta$, using a scan rate of 2° min^{-1} in 0.05° increments and Cu K α radiation (1.542 \AA) operating at 40 kV and 100 mA. The Jade program (Version 3.1 from Materials Data, Inc., Livermore CA) was used to determine the presence of any crystallographic phases in the rice hull ash.

Structure determination: Colorless needles of octasilicate were crystallized from water at $23 \text{ }^\circ\text{C}$. The structure consists of a $[\text{Si}_8\text{O}_{20}]^{-8}$ anion positioned on an inversion center in the crystal lattice.²⁵ The choline cations are located on general positions in the crystal lattice with one being disordered over two positions. Non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. In addition to the hydrogen bonds listed in ref. 25, it is probable that the lattice water molecules are involved in a complex hydrogen bond network. Unfortunately, it was not possible to locate these hydrogen atoms on a difference map and they have not been included.

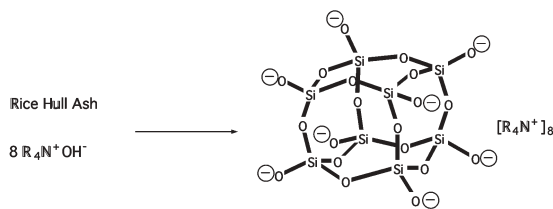
Materials

Rice hull ash with a surface area of $22 \text{ m}^2 \text{ g}^{-1}$ and a TGA ceramic yield of 95 wt.% SiO_2 (remainder carbon) was obtained as a gift from Uncle Ben's[™] USA. X-Ray powder diffraction shows that the rice hull ash is mostly amorphous. MeOH solutions of choline hydroxide (45%) and tetramethylammonium hydroxide (20%, TMAOH) were obtained from Sigma-Aldrich and used without further purification. Methanol and hexane were also obtained from Sigma-Aldrich. Reagent grade HMe_2SiCl was purchased from Gelest.

Standard reaction for RHA dissolution with $[\text{Me}_3\text{NCH}_2\text{-CH}_2\text{OH}]\text{OH}$: Methanolic choline hydroxide solution (218 mL, 1.70 mol) was poured into a 1000 mL flask containing milled rice hull ash (60.491 g, 0.998 mol), methanol (101.4 mL, 1.29 mol) and water (72.0 mL, 4.00 mol) with a magnetic stirrer. The reaction vessel was flushed with nitrogen and reaction mixture stirred at $\approx 21 \text{ }^\circ\text{C}$ from 1–43 days to give dark brown octaanion solutions. Filtration followed by washing with methanol ($3 \times$, 30 mL) gave 375 mL. On solvent removal, white crystals of choline octaanion form that can be recrystallized from hot MeOH or EtOH to prepare crystallographic quality crystals.

Standard reaction for RHA dissolution with choline hydroxide, $[\text{Me}_4\text{N}]\text{OH}$: Identical to the $[\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}]\text{OH}$ studies.

Synthesis of octadimethylsiloxyoctasilsesquioxane (OHS) cube: Me_2SiHCl (21.8 mL, 0.200 mol) and hexane (125.0 mL) are added to a 500 mL Schlenk flask and cooled to $0 \text{ }^\circ\text{C}$ with N_2 . A 50.0 mL octaanion solution is added dropwise over 30 min, and stirred for another 30 min. Separation of the organic phase followed by drying over MgSO_4 and rotary evaporation gives a white, powdery solid (3.82 g, 46.5%). The total yield per reaction solution would be 27.90 g. Kinetic studies were conducted based on these standard reactions for $[\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}]\text{OH}$ and Me_4NOH , as discussed below.



Results and discussion

The work discussed here had several goals. One was to explore the use of RHA as a low-cost starting material for the synthesis of $[NR_4]_8[OSiO_{1.5}]_8$ [Scheme 6] and thereafter the silylated compound, $[HMe_2SiOSiO_{1.5}]_8$ **OHS** [Scheme 7].

In contrast to Schemes 2–5 which give reasonable yields only at temperatures exceeding 150 °C and with constant removal of water, Scheme 6 occurs with considerable facility below 100 °C, even at ambient and preferably with water added, indicating a quite different reaction pathway.

Thus, the work reported here represents the first depolymerization of rice hull ash silica at room temperature with the exclusive formation of octasilicate anions rather than simple silicate anions. Furthermore, it also represents a simple and novel route to polyfunctional silsesquioxanes, which have been used for formulating a wide variety of nanocomposites with complete control of periodicity and with novel, tailorable properties.^{26–28}

The second objective was to determine if this reaction could be done under mild conditions, such as those that might occur in biological environments. Hence, the first sets of kinetic studies were run at ≈ 21 °C in methanolic solutions of choline hydroxide or tetramethylammonium hydroxide as a function of time and reactant concentrations. The resulting octaanion was converted to octadimethylsiloxyoctaasilicate, $[HSiMe_2OSiO_{1.5}]_8$ (**OHS**, see Experimental), at 90+% conversions. The isolated **OHS** yields were used to probe reaction rates and as a measure of octaanion produced. The data for the standard reaction studies are shown in Fig. 2.

Thus, after reaction for 43 days under standard conditions (see Experimental), the **OHS** yield was 48.7% ($\pm 0.2\%$). Stirring for 28 days gave 46.5% ($\pm 0.3\%$) **OHS**, but only 11.0% ($\pm 0.5\%$) after 1 day. In contrast, $Si(OEt)_4$ gives the same products in minutes but is not a natural silica source.²³

The maximum yields obtained at ambient approach $\approx 50\%$, and are commensurate with literature studies on the solubility of silica in rice hull ash. The silica activity index (SAI) parameter, developed by Mehta,²⁹ provides a measure of the amorphous and soluble silica in rice hull ash.¹⁵ The SAI is based on the percentage silica that dissolves in excess boiling

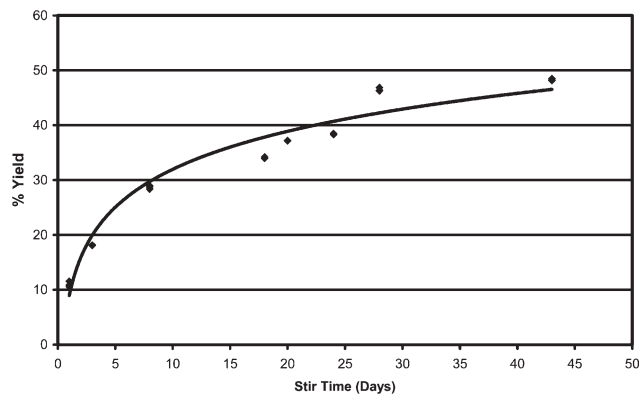


Fig. 2 RHA dissolution rate based on OHS yield vs. time (room temperature). Line added to guide the eye.

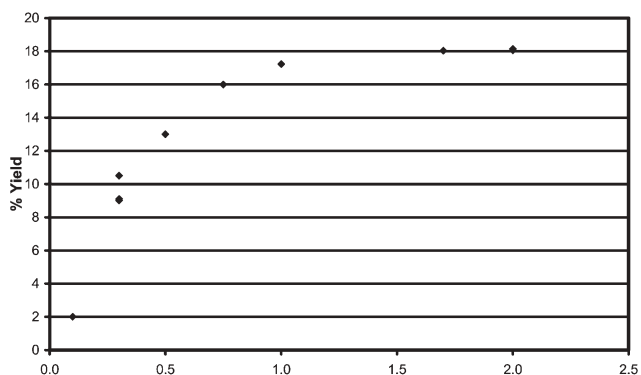


Fig. 3 RHA dissolution as a function of $[Me_4NOH]$ at 21 °C for 3 days. Standard deviation limits within width of data points.

0.5 M NaOH under specified conditions. Boateng and Skeete report³⁰ that rice hull ash of varying color, resulting from differing furnace temperatures and burn durations, has SAI values that correspond with color. Ash that is darker in color (gray to light gray) displays lower SAI values, from 50–65%, whereas white ash has values near 70%. Given that the ash used here is dark grey, the 50% maximum **OHS** yields are consistent with the observations of Boateng and Skeete.

Dissolution as a function of base concentration

Fig. 3 records studies on the rate of dissolution (three day reaction times) as a function of Me_4NOH concentration. The Fig. 3 rates of dissolution appear to asymptote just above 1 equivalent of base. Basically, these results indicate that the reaction is not catalytic in Me_4NOH , as found for Scheme 5, and suggest that the Me_4N (or $Me_3NCH_2CH_2OH$) cations are necessary to the formation and/or stabilization of the

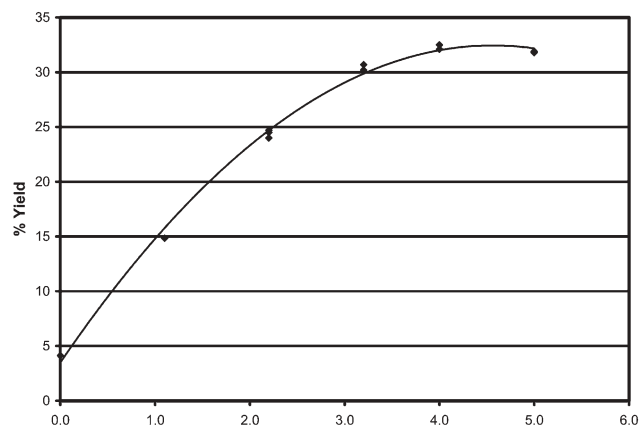


Fig. 4 [Me₄N]OH promoted RHA dissolution vs. mol H₂O per mol SiO₂ for 18 days.

octasilicate anion. A further observation is that even at low [Me₄NOH], octaanion forms, suggesting the potential to form under conditions that are not strongly basic as in biological environments. Likewise, water is found to be necessary.

Dissolution as a function of water concentration

Hasegawa *et al.* find that the reaction of Me₄NOH with Si(OEt)₄ with excess water is highly selective for formation of [OSiO_{1.5}]₈.^{23,24} Thus, we examined the effects of water concentration on the rate of formation of the octasilicate as shown in Figs. 4 and 5. These data indicate that water is essential to the formation of both [R₄N]₈[OSiO_{1.5}]₈ (R = Me, CH₂CH₂OH) in contrast to Schemes 1–5. Under the conditions used here maximum yields are obtained when 3.0 equivalents per equivalent of SiO₂ are used for the choline hydroxide reaction and ≈5 equivalents per equivalent of SiO₂ when [Me₄N]OH is used as base.

Dissolution as a function of temperature

The use of ambient temperatures to study the above reactions, while perhaps valuable in considering octaanion formation during biosilicification processes, is not valuable from a practical standpoint. Consequently, a last set of studies was done to study temperature effects on RHA dissolution as presented in Fig. 6.

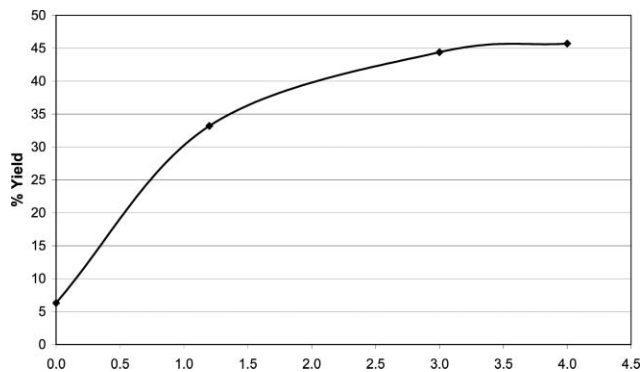


Fig. 5 [Me₃NCH₂CH₂OH]OH promoted RHA dissolution vs. mol H₂O per mol SiO₂ under standard conditions (43 days).

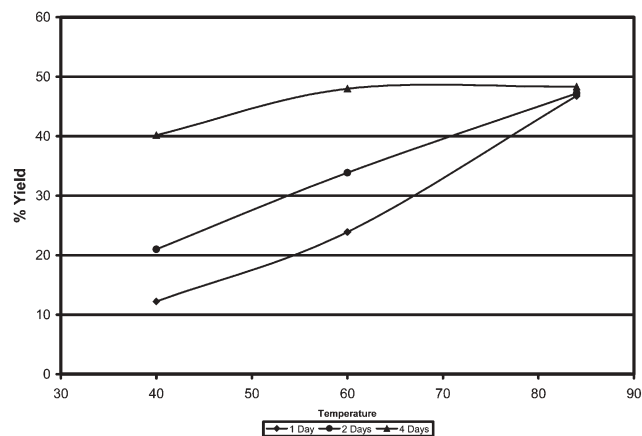


Fig. 6 Yield vs. temperature for RHA dissolution using standard conditions.

Clearly, the rates of dissolution can be increased to the point where the reaction is over in 1 day at 80 °C (reflux). Since these reactions are done at 60 g scales, it is possible to synthesize 10–12 g quantities of OHS very easily in a short period indicating that the RHA route to OHS is practical.

The Fig. 6 (two day) data were used to calculate the activation energy for dissolution for the [Me₄N]OH system. Relying on the lower reaction times to ensure that silica dissolution rates were less susceptible to changes in surface area of available silica, values of E_a for dissolution were determined to be 5 ± 1 kcal mol⁻¹ which differs significantly from the other studies noted above where E_a was typically in the 12–15 kcal mol⁻¹ range. We will comment about this below after a brief discussion of the crystal structure of the choline octasilicate.

Choline octasilicate structure

Single crystals of the choline octasilicate were isolated and an X-ray structural determination carried out (Fig. 7). The bond lengths and bond angles of the cage structure are in keeping with previously published structures.^{31–33} Of particular importance here are the waters of hydration/crystallization. Waters of hydration are common features of octasilicate structures with amounts ranging from 5 to 100 for the set of octasilicate structures reported. For example, single crystal studies of [Me₄N]₈[OSiO_{1.5}]₈ reveal 65 tightly bound waters of hydration³¹ or approximately 8 H₂O per SiO_{1.5} unit. The crystal structure of the choline octaanion, Fig. 7, has 24 waters per octaanion or 3.0 H₂O per SiO_{1.5} unit.

In these systems, the Si–O⁻ anion is so weakly basic that it does not easily deprotonate water. However, in acidic environments, stable octasilicate cages with Si–OH moieties do form^{32,33} as seen in the crystal structure of [N(nC₄H₉)₄]H₇[Si₈O₂₀]·5.33H₂O, wherein seven of the eight Si–O⁻ anions are protonated. Note that here there are only five waters of hydration total or less than one per SiO_{1.5} unit.

Dissolution processes, rate data and mechanisms of octaanion formation

RHA is not a homogeneous silica material. It consists of microporous, incompletely amorphous silica mixed with

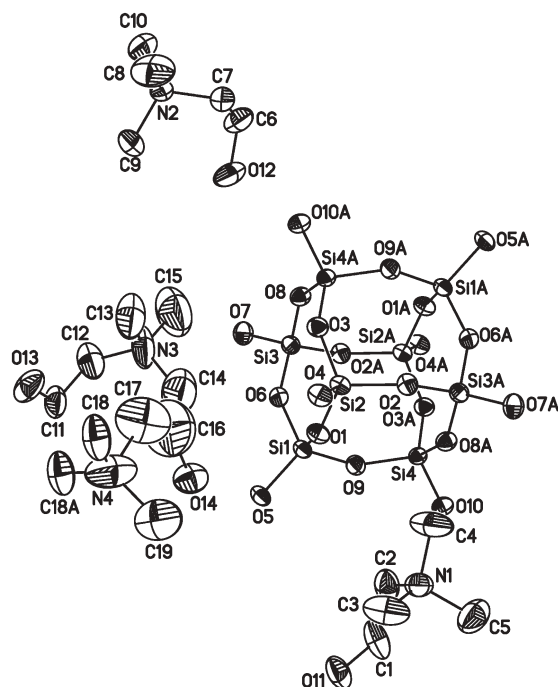


Fig. 7 Single crystal X-ray structure of $[\text{OSiO}_{1.5}]_8[\text{Me}_3\text{NCH}_2\text{-CH}_2\text{OH}]_8 \cdot 24\text{H}_2\text{O}$. Waters of crystallization and additional cholines not shown to provide a better view of the octaanion (see Experimental and Electronic Supplementary Information (ESI)[†]).

random particles of amorphous carbon. Consequently, it is difficult to make pointed statements about the mechanisms controlling dissolution. However, some general observations can be made.

We can begin with the rate of dissolution at room temperature as a function of time. The first data point for dissolution after one day is 11% conversion. Thus, >20% of all the silica that will dissolve after 43 days does so in 24 h at ambient. Recall that this conversion is measured as isolated OHS derived from the octaanion, which will not form without an ammonium cation.^{23,24} Thus, there is no “blank” dissolution component to measure. This point is supported by the Fig. 3 data where; as the Me_4NOH concentration goes to zero, as does conversion to OHS. Consequently, we can assume that depolymerization is actually very fast at ambient and probably is not the rate-controlling step. If so, then what are the first products in solution?

A number of studies, especially by ^{29}Si NMR, have examined the solution behavior of sodium and alkylammonium silicates.²³ In general for sodium silicates; monomers, dimers and cyclic trimers are observed. Competition between sodium and alkylammonium counter ions indicates that at high sodium : alkylammonium ratios, typical sodium dominated species form. At low alkylammonium concentrations (without sodium) the same species are observed. However, at higher concentrations (0.5–1.0 M), the octaanion is the sole species observed. Thus, R_4NOH promoted silica dissolution likely first generates monomeric species otherwise higher order rate dependence on concentration might be expected. Thereafter, condensation to the octaanion appears rapid but still can be the rate determining step.

The high isolated yields of OHS, coupled with the absence by GPC of any other products, points to the octaanion being formed rapidly to the exclusion of other species, including the hexaanion, which forms exclusively for Et_4N^+ or nBu_4N^+ counterions.³⁴

Hasegawa *et al.* suggest that the high degree with which water orders around tetraalkylammonium ions in aqueous solutions^{23,24} acts to template octaanion formation. Both results are in keeping with the amounts of water that optimize dissolution of silica (or the formation of the octaanion, see below) in Figs. 4 and 5. Given that water enhances yields and imparts stability to the $[\text{R}_4\text{N}]_8[\text{OSiO}_{1.5}]_8$ systems, this suggests these species may be stable in aqueous environments, as discussed below.

The dissolution rate dependence on $[\text{R}_4\text{NOH}]$ (Fig. 3) indicates the absence of catalytic dissolution. This in turn suggests that R_4N^+ , once reacted with silica, stays with the silicate anion and is somehow involved in the slow step. Likewise, the water concentration effects also suggest that water is necessary to the slow step. It seems reasonable to consider the assembly of eight hydrated ammonium silicate species, into a single octaanion, the rate-controlling step(s).

The condensation of silanol species leading to the formation of dimers, trimers and rings has been modelled in some detail by Gordon and Kudo.³⁵ McCormick *et al.* have considered the formation of cyclic species including cubic silsesquioxanes in modelling sol–gel condensation processes leading to gelation.³⁶ The latter work finds that the silsesquioxane formation as a component of gelation provides a better fit to observed processes than if it is ignored.

The modelling studies of Gordon and Kudo are very important for several reasons. First they calculate 7–10 kcal mol⁻¹ barriers to the processes wherein silanol species condense to form dimers, trimers, cyclic trimers and tetramers. However, the introduction of water eliminates all barriers to the condensation process, indeed these studies suggest it is highly favorable with E_a values now ≤ -10 kcal mol⁻¹. This is in keeping with our experimental results, which show a small, 5 ± 1 kcal mol⁻¹, barrier for the formation of octaanion and a strongly promoting effect by water, as predicted. One might argue that the small barrier to formation found here differs from the thermodynamically very favorable processes found by Gordon and Kudo because the condensation processes here involve anionic silanols that can be expected to exhibit some repulsive forces. Alternately or additionally the reordering of R_4N^+ species around the anion during condensation processes may also contribute to the small barrier observed.

Whatever these minimal barriers are, it is clear that octaanion formation in aqueous alcoholic environments is highly favored to the exclusion of all other silicate species, especially in the presence of ammonium cations. Furthermore, based on the work reported here, previous efforts by Hoebbel *et al.*,³⁷ Hasegawa *et al.*,^{23a,b} Harrison *et al.*,^{23c,34} and several other research groups, it appears that octasilicate and cubic silsesquioxanes form in many environments and are likely key intermediates in the formation of many types of silane sol–gel processes.³⁶ In addition, they appear to be common intermediate species formed in zeolite syntheses, especially amine templated syntheses.^{38,39} The facility with which they

form, especially at high silicate anion concentrations and at ambient temperatures suggests that they may form in nature. Indeed, there are some reports on the biosilicification process that lend credence to this idea.^{41–47}

The choline structure is reminiscent of hydroxyamino acids found in sponge filament proteins.^{41,42,44–47} It is also one end of ϵ -*N,N,N*-trimethyl- γ -hydroxylysine found in silafins,^{46,47} a group of polycationic peptides isolated from diatoms and identified as likely sites for silica precipitation in SDV. Silafins also contain 6–11 *N*-methylpropylamine oligomers, which strongly resemble triethylenetetraamine. These observations suggest that octasilicates or silsesquioxanes may be the missing components in at least some biosilicification processes.

The processes whereby inorganic silica present in the environment, typically as silicic acid $[\text{Si}(\text{OH})_4]$, becomes incorporated in plant and animal life especially in the intricate structures found in diatoms has been the subject of extensive discussion in the literature for many years.^{41,42} This discussion has intensified recently as these processes may offer potential for the low temperature construction of complex micro and nanostructures for nanotechnology⁴³ and for energy efficient and “green” chemical processing of silica.

The commonly accepted biosilicification mechanism, studied most completely for diatoms, involves the extraction of ppm concentrations of silicic acid from water at near neutral pHs followed by concentration at levels of up to ≈ 0.5 M in “silica transport/deposition vesicles” (STV/SDV). Thereafter, the soluble silica is polymerized, precipitated and directed towards “construction sites.”^{41–47} A key unanswered question in these studies concerns the form the extracted silicic acid takes during concentration, transport and storage prior to being deposited at neutral or slightly acidic pHs.

Although studied extensively there is currently no resolution to this problem. It has been suggested that the silica is stored through formation of neutral species with Si–O–C bonds.⁴⁸ Alternate proposals suggest that silica is transported and stored as penta- and/or hexacoordinated species (with Si–O–C bonds) formed between certain sugars and silica or silicic acid.^{49,50} However, still other studies find no support for the formation of Si–O–C species⁴⁹ and theoretical calculations suggest that hypercoordination may be thermodynamically less favored in biological environments than tetracoordinated silicon.⁵¹

Our current studies may offer insight into the processes whereby organisms such as diatoms acquire silicic acid from aqueous environments at nearly neutral pH's, transport and store silica in an aqueous form at concentrations 0.1–0.5 M in a form amenable to rapid polymerization.

The key points regarding the relationship of $[\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}]_8[\text{OSiO}_{1.5}]_8$ to biosilicification processes are as follows. The compound forms easily and quantitatively at ambient temperatures. The choline structure is very similar to that of ϵ -*N,N,N*-trimethyl- γ -hydroxylysine, to the oligomeric *N*-methylpropylamine components found in silafins, and to the hydroxyamino acid units found in sponge filament proteins. Given that Hildebrand *et al.* demonstrated⁴² that unionized silicic acid is first transported across cell wall membranes and into the cell, it seems most likely that octaanion formation with possible partial protonation could

occur thereafter to stabilize some form of octasilicate species for transport and eventually catalyze its polymerization during a deposition event.

This concept is further supported by the fact that optimal conversion of soluble silica species to the very stable octaanion structure occurs at concentrations ≥ 0.3 M,^{47,50} levels close to those in STV and SDV. As we will show in a later paper,⁴⁰ these structures are so stable that the alkylammonium octaanion systems cannot exchange with water molecules to form Si–OH groups (under basic conditions) coincidentally regenerating R_4NOH , which would lead to catalytic dissolution of silica as we have seen with other types of bases including triethylenetetraamine.

Again, as noted above, several crystal structures of $[\text{OSiO}_{1.5}]_8$ cages find waters of hydration ranging from 100 to the 24 noted here. In these systems, the oxygen anion is so stable that it does not deprotonate these waters. Furthermore even in acidic environments, stable octasilicate cages with Si–OH form, $[\text{N}(n\text{C}_4\text{H}_9)_4]\text{H}_7[\text{Si}_8\text{O}_{20}] \cdot 5.33\text{H}_2\text{O}$.³³ In this crystal structure, hydrogen bonding between Si–OH groups is sufficiently strong as to form a structural framework similar to those found in zeolites. More important, this structure offers a possible picture of intermediates that would form in polymerization processes in the SDV. The fact that these species are sufficiently stable to grow crystals large enough for single crystal studies suggests that they are stable at ambient and could be transported and/or stored *in vivo*.

One might argue that our starting conditions, 4.5 M in R_4NOH , are far from the conditions expected in a biological environment. However, we note that the reactant here is silica rather than silicic acid, and when $\text{Si}(\text{OEt})_4$ is used the reaction takes only minutes at ambient.^{47,50} The final “pH” in our alcoholic solutions is approximately 8 (when one equivalent of R_4NOH is used per soluble silica), and suggests that these species could indeed be present in near neutral environments. Furthermore, the fact that silafins have oligomer chains consisting of 6–11 *N*-methylpropylamine units argues that a highly basic environment can exist in a biological environment. The pKb_1 of triethylenetetraamine, $\text{H}[\text{HNCH}_2\text{CH}_2]_3\text{NH}_2$ is 3.21. The pKb_1 of $[\text{MeNCH}_2\text{CH}_2\text{CH}_2]_{6-11}$ is likely much lower and in the microenvironment of an STV/SDV, the pH could be much higher than anticipated. Given the presence of serine hydroxyl groups in close proximity, it seems reasonable to argue that octasilicate or silsesquioxane species should readily form in STVs and SDVs. Given the numbers of hydroxyl moieties in the STV/SDV environments, it seems reasonable to suggest that the formation of the octasilicate anion in an aqueous alcoholic media such as used here may actually be more representative of these environments than one that is purely aqueous. *In toto* there is sufficient reason to believe that octasilicate anions can form in biological environments and may indeed be a key SiO_x species in the biosilicification process.

In closing, we note that the octaanion can be made simply and in high yield from rice hull ash, a waste product produced in 10 000 tons per year quantities, and is easily converted to **OHS** in high yield. **OHS** is the basis for libraries of polyfunctional nanobuilding blocks that can be processed to unique hybrid nanocomposites wherein the periodicity of the

hard particles and soft organic tethers are completely defined, as are the macroscopic properties derived therefrom.^{24–28}

Acknowledgements

We would like to thank Professor Galen Stucky for drawing our attention to the papers by Weibcke and Lebau. We would also like to thank Professor Daniel Morse for helpful comments and explanations concerning our work and the biosilicification process. This work was funded in part by the FAA, NSF and the Air Force Office of Scientific Research.

M. Z. Asuncion,^b I. Hasegawa,^d J. W. Kampf^a and R. M. Laine^{*bc}

^aDept. of Chemistry, University of Michigan, Ann Arbor, MI 48109-2136, USA

^bMacromolecular Science and Engineering Program, University of Michigan, Ann Arbor, MI 48109-2136, USA.

E-mail: talsdad@umich.edu

^cDept. of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA

^dDept of Chemistry, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu 501-1193, Japan

References

- 1 D. S. Chaudry and M. C. Jollands, *J. Appl. Polym. Sci.*, 2004, **93**, 1–8.
- 2 J. C. C. Freitas, F. G. Emmerich and T. J. Bonagamba, *Chem. Mater.*, 2000, **12**, 711–718.
- 3 H. Teng, H.-C. Lin and J.-A. Ho, *Ind. Eng. Chem. Res.*, 1997, **36**, 3974–3977.
- 4 L. Sun and K. Gong, *Ind. Eng. Chem. Res.*, 2001, **40**, 5861–5877.
- 5 *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley-Interscience, New York, 3rd edn. 1979, vol. 20, pp 750–880.
- 6 A. Rosenheim, B. Raibmann and G. Z. Schendel, *Z. Anorg. Allg. Chem.*, 1931, **196**, 160.
- 7 D. W. Barnum, *Inorg. Chem.*, 1970, **9**, 1942; D. W. Barnum, *Inorg. Chem.*, 1970, **11**, 1424–1426.
- 8 A. Weiss, G. Reiff and A. Z. Weiss, *Z. Anorg. Allg. Chem.*, 1961, **311**, 151–179.
- 9 C. L. Frye, *J. Am. Chem. Soc.*, 1964, **86**, 3170.
- 10 F. P. Boer, J. J. Flynn and J. W. Turley, *J. Am. Chem. Soc.*, 1968, **90**, 6973; J. J. Flynn and F. P. Boer, *J. Am. Chem. Soc.*, 1969, **91**, 5756.
- 11 A. Boudin, G. Cerveau, C. Chuit, R. J. P. Corriu and C. Reye, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 473–474.
- 12 R. J. P. Corriu and J. C. Young, in *Chemistry of Organic Silicon Compounds*, ed. S. Patai, Z. Rappaport, Wiley-Interscience, New York, 1989, ch. 20; R. J. P. Corriu, *Pure Appl. Chem.*, 1988, **60**, 99–106.
- 13 D. L. Bailey, A. Snyder and F. M. O'Connor, US Patent 2,881,198, 1959.
- 14 M. E. Kenney and G. B. Goodwin, US Patent 4,717,773, 1988; M. E. Kenney and G. B. Goodwin, in *Inorganic and Organometallic Polymers ACS Symposium Series*, ed. M. Zeldin, K. J. Wynne, American Chemical Society, Washington, DC, 1988, vol. 360, p. 238; G. B. Goodwin and M. E. Kenney, *Adv. Chem. Ser.*, 1990, **224**, 251.
- 15 E. Suzuki, M. Akiyama and Y. Ono, *J. Chem. Soc., Chem. Commun.*, 1992, **2**, 136–137.
- 16 L. N. Lewis, F. J. Schattenmann, T. M. Jordan, J. C. Carnahan, W. P. Flanagan, R. J. Wroczynski, J. P. Lemmon, J. M. Anostario and M. A. Othon, *Inorg. Chem.*, 2002, **41**, 2608–2615 and references therein.
- 17 R. M. Laine, K. Y. Blohowiak, T. R. Robinson, M. L. Hoppe, P. Nardi, J. Kampf and J. Uhm, *Nature*, 1991, **353**, 642–644.
- 18 M. L. Hoppe, R. M. Laine, J. Kampf, M. S. Gordon and L. W. Burggraf, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 287–289.
- 19 H. Cheng, R. Tamaki, R. M. Laine, F. Babonneau, Y. Chujo and D. R. Treadwell, *J. Am. Chem. Soc.*, 2000, **122**, 10063–10072.
- 20 H. Cheng and R. M. Laine, *New J. Chem.*, 1999, **23**, 1181–1189.
- 21 R. L. Stone and T. D. Tieman, *Trans. Soc. Miner. Eng.*, 1964, June, 217–222 and references therein.
- 22 T. D. Tieman, *Trans. Soc. Miner. Eng.*, 1964, Sept., 258–259.
- 23 I. Hasegawa, S. Sakka, K. Kuroda and C. Kato, *J. Mol. Liq.*, 1987, **34**, 307–315; I. Hasegawa, S. Sakka, K. Kuroda and C. Kato, *Bull. Inst. Chem. Res. Kyoto, Univ.*, 1997, **65**, 192–196; R. K. Harris and C. T. G. Knight, *J. Mol. Struct.*, 1982, **78**, 273–278.
- 24 I. Hasegawa and S. Sakka, in *Zeolite Synthesis ACS Symposium Series*, ed. M. L. Ocelli, H. E. Robson, American Chemical Society, Washington, DC, 1989, Vol. 398, pp 140–151; I. Hasegawa and S. Sakka, *Chem. Lett.*, 1988, **8**, 1319–1322.
- 25 Chemical formula: C₄₀H₁₆₀N₈O₅₂Si₈; Formula weight: 1810.48; Unit-cell dimensions: $a = 11.9649(9) \text{ \AA}$, $\alpha = 90^\circ$, $b = 16.5185(12) \text{ \AA}$, $\beta = 90.8860(10)^\circ$, $c = 20.8305(16) \text{ \AA}$, $\gamma = 90^\circ$; Volume: 4116.5(5) \AA^3 ; Temperature: 158(2) K; Space group: $P2(1)/n$; $Z = 2$, $\mu = 0.237 \text{ mm}^{-1}$; Number of reflections measured = 40536, independent reflections = 8427; $R(\text{int}) = 0.0440$, R indices (all data): $RI = 0.0973$, $wR2 = 0.2294$.
- 26 R. M. Laine, J. Choi and I. Lee, *Adv. Mater.*, 2001, **13**, 800–803; J. Choi, J. Harcup, A. F. Yee, Q. Zhu and R. M. Laine, *J. Am. Chem. Soc.*, 2001, **123**, 11420–11430.
- 27 J. Choi, A. F. Yee and R. M. Laine, *Chem. Mater.*, 2003, **15**, 5666–5682.
- 28 J. Choi, A. F. Yee and R. M. Laine, *Macromol.*, 2004, **37**, 3267–3276.
- 29 K. P. Mehta, in *Proc. UNIDO/ESCAP/RCTT Workshop on Rice Husk Ash Cement*, Regional Centre For Technology Transfer, Bangalor, India, 1979, pp 113–122.
- 30 A. Boateng and D. Skeete, *Cem. Concr. Res.*, 1990, **20**, 795–802.
- 31 M. Wiebcke, M. Grube, H. Koller, G. Engelhardt and J. Felsche, *Microporous Mater.*, 1993, **2**, 55–63.
- 32 M. Wiebcke, J. Emmerich and J. J. Felsche, *J. Chem. Soc., Chem. Commun.*, 1993, **21**, 1604–1606.
- 33 G. Bissert and F. Liebau, *Z. Kristallogr.*, 1987, **179**, 357–371.
- 34 P. G. Harrison, R. Kannengiesser and C. J. Hall, *Main Group Met. Chem.*, 1997, **20**, 137–141 and references therein.
- 35 T. Kudo and M. Gordon, *J. Phys. Chem. A.*, 2002, **106**, 11347–11353; T. Kudo and M. Gordon, *J. Phys. Chem. A.*, 2000, **104**, 4058–4063; T. Kudo and M. Gordon, *J. Am. Chem. Soc.*, 1998, **120**, 11432–11438.
- 36 S. E. Rankin, L. J. Kasehagen, A. V. McCormick and C. W. Macosko, *Macromol.*, 2000, **33**, 7639–7648.
- 37 D. Hoebbel, I. Pitsch, T. Reiher, W. Hiller, H. Jancke and D. Muller, *Z. Anorg. Allg. Chem.*, 1989, **576**, 160–168; D. Hoebbel, K. Endres, T. Reinert and I. Pitsch, *J. Non-Cryst. Solids*, 1994, **176**, 179–188.
- 38 A. Firouzi, F. Atef, A. G. Oertli, G. D. Stucky and B. F. Chmelka, *J. Am. Chem. Soc.*, 1997, **119**, 3596–3610.
- 39 A. Firouzi, D. J. Schaefer, S. H. Tolbert, G. D. Stucky and B. F. Chmelka, *J. Am. Chem. Soc.*, 1997, **119**, 9466–9477.
- 40 H. Kang and R. M. Laine, unpublished work.
- 41 C. C. Perry and T. J. Keeling-Tucker, *J. Biol. Inorg. Chem.*, 2000, **5**, 537–550.
- 42 V. Martin-Jesequel, M. Hildebrand and M. A. Brzezinski, *J. Phycol.*, 2000, **36**, 821–840.
- 43 J. Parkinson and R. Gordon, *Trends Biotechnol.*, 1999, **17**, 190–196.
- 44 J. N. Cha, G. D. Stucky, D. E. Morse and T. J. Deming, *Nature*, 2000, **403**, 289–292.
- 45 Y. Zhou, K. Shimizu, J. N. Cha, G. D. Stucky and D. E. Morse, *Angew. Chem., Int. Ed.*, 1999, **38**, 781–782.
- 46 N. Kröger, R. Duetzmann and M. Sumper, *Science*, 1999, **286**, 1129–1132.
- 47 N. Kröger, R. Duetzmann and M. Sumper, *J. Biol. Chem.*, 2001, **276**, 26066–26070.
- 48 K. Schwartz, *Proc. Natl. Acad. Sci. USA*, 1973, **70**, 1606–1612.
- 49 C. C. Perry and S. Mann, in *Origin, Evolution and Modern Aspects of Biomineralization in Plants and Animals*, ed. R. E. Crick, Plenum Press, New York, 1989, pp 419–431.
- 50 S. D. Kinrade, J. W. Del Nin, A. S. Schach, T. A. Sloan, K. L. Wilson and C. T. G. Knight, *Science*, 1999, **285**, 1542; J. B. Lambert, G. Lu, S. R. Singer and V. M. Kolb, *J. Am. Chem. Soc.*, 2004, **126**, 9611–9625.
- 51 N. Sahai, *Geochim. Cosmochim. Acta*, 2004, **68**, 227–237 and references therein.