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Chemical Geology 199 (2003) 83–90

CHEMICAL GEOLOGY
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# The effect of cyanobacteria on silica precipitation at neutral pH: implications for bacterial silicification in geothermal hot springs

Nathan Yee[a,*], Vernon R. Phoenix[b], Kurt O. Konhauser[c], Liane G. Benning[a], F. Grant Ferris[b]

[a] *School of Earth Sciences, University of Leeds, Leeds, LS2 9JT, United Kingdom*
[b] *Department of Geology, The University of Toronto, 22 Russell Street, Toronto, Ontario, Canada M5S 3B1*
[c] *The Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, Canada T6G 2E3*

Received 13 March 2002; accepted 18 February 2003

**Abstract**

In this study, we performed silica precipitation experiments with the cyanobacteria *Calothrix* sp. to investigate the mechanisms of silica biomineralization. Batch silica precipitation experiments were conducted at neutral pH as a function of time, Si saturation states, temperature and ferrihydrite concentrations. The experimental results show that in solutions undersaturated with respect to amorphous silica, the interaction between Si and cell surface functional groups is weak and minimal Si sorption onto cyanobacterial surfaces occurs. In solutions at high Si supersaturation states, abiotic Si polymerization is spontaneous, and at the time scales of our experiments (1–50 h) the presence of cyanobacteria had a negligible effect on silica precipitation kinetics. At lower supersaturation states, Si polymerization is slow and the presence of cyanobacteria do not promote Si–solid phase nucleation. In contrast, experiments conducted with ferrihydrite-coated cyanobacteria significantly increase the rate of Si removal, and the extent to which Si is removed increases as a function of ferrihydrite concentration. Experiments conducted with inorganic ferrihydrite colloids (without cyanobacteria) removes similar amounts of Si, suggesting that microbial surfaces play a limited role in the silica precipitation process. Therefore, in supersaturated hydrothermal waters, silica precipitation is largely nonbiogenic and cyanobacterial surfaces have a negligible effect on silica nucleation.


*Keywords:* Cyanobacteria; Silica precipitation; Hot springs

## 1. Introduction

Cyanobacterial silicification is an important geological process in modern geothermal environments which can affect microbial fossilization, chemical sediment formation, and Si transport in geothermal hot springs (Schultze-Lam et al., 1995; Jones et al., 1997; Konhauser et al., 2001). Field-based studies of modern siliceous sinter deposits in Iceland, Yellowstone (USA), and New Zealand have found filamentous cyanobacteria coated in siliceous precipitates (Ferris et al., 1986; Schultze-Lam et al., 1995; Konhauser and Ferris, 1996; Jones et al., 1997, 1999; Konhauser et al., 2001). However, microbial silicification mechanisms are poorly understood, and it is unknown if the driving forces underpinning biomineralization is the cooling and evaporation of the supersaturated waters, or if it is

* Corresponding author. Tel.: +44-113-343-6623.
*E-mail address:* nyee@earth.leeds.ac.uk (N. Yee).

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doi:10.1016/S0009-2541(03)00120-7

biogenically mediated, due to heterogeneous nucleation of amorphous silica on microbial surfaces.

Several experimental studies performed under laboratory conditions have attempted to elucidate the processes involved in the silicification of organic material. Early laboratory studies suggested that aqueous silica is heterogenously precipitated onto organic surfaces via hydrogen bonding (e.g. Leo and Barghoorn, 1976; Westall et al., 1995) or sorption of negatively charged silica ions to positively charged surface functional groups (Urrutia and Beveridge, 1993). In contrast, the experimental results of Heaney and Yates (1998) indicated that in saturated solutions amorphous silica precipitated homogeneously, and it is the polymeric/colloidal silica fraction which deposits onto organic surfaces. Similarly, Walter et al. (1972) suggested that silica precipitation in hot springs is an inorganically controlled process, induced by rapid cooling and evaporation of the spring water after expulsion from the vent, and occurs independent of microorganisms.

Previous studies have also suggested that the association between silicate minerals and bacterial surfaces is not caused by direct Si–bacteria interactions (e.g. Konhauser et al., 1993, 1994; Urrutia and Beveridge, 1994). A study by Fein et al. (2002) demonstrated that silica binding onto *Bacillus subtilis* surfaces is weak, and that even at dilute concentrations, Si displays a low affinity for bacterial cell walls. Conversely, ferrihydrite-coated bacteria bind significant concentrations of Si, suggesting that Fe plays an important role in the formation of silicate biominerals. However, all experiments by Fein et al. (2002) were conducted in solutions undersaturated with respect to all Si-bearing mineral phases, and it is unclear if bacterial surfaces can affect the precipitation kinetics of silica in supersaturated fluids.

In solutions supersaturated with respect to amorphous silica, it has been proposed that microorganisms can directly bind and nucleate silicate ions to form heterogeneously precipitated silica aggregates (Ferris et al., 1986, 1988; Urrutia and Beveridge 1993). In order to determine the role of bacteria on silica precipitation in acidic mine tailings, Fortin and Beveridge (1997) conducted laboratory and field investigations with the acidophilic bacteria *Thiobacillus*. At low pH conditions, the polymerization of monosilicic acid ($H_4SiO_4$) is slow, and kinetic activation energy barriers inhibit silica nucleation (Iler, 1979; Makrides et al., 1980; Weres et al., 1981). Fortin and Beveridge (1997) demonstrated at the presence of *Thiobacillus* promoted rapid formation of amorphous silica at low pH values, while an abiotic system with the same chemical conditions did not show silica precipitation. Therefore in acidic solutions, the presence of bacteria can act as a reactive interface that facilitates heterogeneous nucleation and enhances the precipitation kinetics. However, in hot spring environments, the pH values are commonly near neutral, and the nucleation and polymerization behaviour of aqueous Si is markedly different. At pH 7, monomeric Si can polymerize to form silica colloids (1–100 nm in diameter) and the polymerization reaction rapidly decreases the concentration of soluble Si in solution (Iler, 1979). Under these conditions, it is unknown if microbial surfaces will enhance silica precipitation by providing additional nucleation sites or if the microorganism act as passive precipitation surfaces.

In this study, we performed silica precipitation experiments with the microogranism *Calothrix* sp. strain KC97 to investigate the role of cyanobacteria in silica mineral formation at neutral pH conditions. Batch silica precipitation experiments were conducted as a function of time, Si saturation states, temperature, and ferrihydrite concentrations. The objectives of this research were to: (1) test if specific surface binding sites on cyanobacterial surfaces facilitate heterogeneous nucleation of silica, and (2) to determine the effect of ferrihydrite-coated cyanobacteria on silica precipitation. This study aims to resolve whether microorganisms are instrumental to silica precipitation, or whether silica precipitation and biomineralization simply occur as a result of inorganic influences.

## 2. Experimental procedures

### 2.1. Cyanobacterial growth and preparation

The cyanobacteria *Calothrix* sp. strain KC97 was isolated from silica sinters adjacent to the Krisuvik hot spring vent, Iceland (Phoenix et al., 2000; Konhauser et al., 2001). This cyanobacteria forms trichomes up to 1 mm long that are surround by a thick polysaccharide sheath (up to 5 μm in thickness). The filaments were cultured in autoclaved liquid BG11 + n media under an

average light irradiance of 700 lx. BG11 is composed of 1500 ppm $NaNO_3$, 40 ppm $K_2HPO_4 \cdot 3H_2O$, 75 ppm $MgSO_4 \cdot 7H_2O$, 36 ppm $CaCl_2 \cdot 2H_2O$, 6 ppm citric acid, 6 ppm ferric ammonium citrate, 1 ppm EDTA, 20 ppm $Na_2CO_3$, 2.9 ppm $H_2BO_3$, 1.8 ppm $MnCl_2 \cdot 4H_2O$, 0.2 ppm $ZnSO_4 \cdot 7H_2O$, 0.4 ppm $NaMoO_4 \cdot 2H_2O$, 0.08 ppm $CuSO_4 \cdot 5H_2O$, 0.05 ppm $Co(NO_3)_2 \cdot 6H_2O$. After growing for approximately 3 weeks, the colonies were carefully homogenized in a tissue grinder with teflon pestle for 5 min to break up clusters of filaments. Homogenization was performed to allow pipetting of equal quantities of filaments into the reaction vessels, thus ensuring an even surface area of cyanobacteria was available. After homogenization, the cells were examined with light microscopy to ensure the clusters were broken but the cells and filaments remained intact. The cyanobacteria suspension was then diluted with BG11 + n media to a final Optical Density at 720 nm ($OD_{720}$) of 0.75. All experiments were conducted in the media solution with living cells.

### 2.2. Silica sorption/precipitation experiments

Batch sorption/precipitation reactions were performed by combining a known amount of Si (from a 300 ppm Si stock solution of $Na_2SiO_3 \cdot 5H_2O$ at pH 12) with the cyanobacterial suspension resulting in a final optical density of $OD_{720} = 0.35$. The pH of the solution was then immediately adjusted to pH $7.0 \pm 0.5$ with 2 M HCl. This neutralization process causes an increase in the saturation index of the solution and induces Si polymerization. At regular intervals, the pH of the solution was measured and the batch reactor was sampled for Si analysis. The drift in pH during the experiment was less than 0.5 pH units. Each sample was centrifuged at 5000 rpm for 1 min to pellet the cyanobacteria, and the eluent was filtered through 0.2 μm cellulose acetate filters (Nalgene). The viability of the cyanobacterial cells after experimentation was confirmed by analysing phycoeyrthrin autofluorescence (this phycobilin is dispersed rapidly upon cell lysis) using a Nikon Microphot-FXA fluorescence microscope. Samples were also taken and fixed in 2.5% glutaraldehyde for transmission electron microscopy (TEM) and selected area electron diffraction (SAED) analysis. The concentration of monomeric Si in the eluent was determined using a molybdate yellow technique (Govett, 1961). The analysis was performed by mixing 1 ml of the sample to 10 ml of 1 N $H_2SO_4$, followed by 10 ml of 0.3 M ammonium molybdate. The sample was allowed to react for 5 min and then was measured at 400 nm with a UV/VIS spectrophotometer. The analysis was calibrated using standards prepared from a 300 ppm Si stock solution. The analytical uncertainty determined for this technique was $\pm 4\%$ ($2\sigma$). Abiotic control experiments were also performed under the identical conditions but in the absence of cyanobacteria.

### 2.3. Silica precipitation by cooling

Silica precipitation experiments were also conducted by cooling a heated solution. In these experiments, 225 ml of 330 ppm stock Si solution was prepared and neutralized to pH 7 with 2 M HCl. The solution was then stored in an oven and allowed to equilibrate for 24 h at 77 °C. After 24 h, the solution was removed from the oven and 25 ml of homogenized *Calothrix* (suspended in BG11 + n at an optical density of 1.1 at 720 nm) was immediately added to the Si solution (this addition diluted the Si concentration to 300 ppm Si). This Si–cyanobacterial suspension was then allowed to cool. At regular intervals, the temperature, pH and aqueous silica concentration was measured. The cyanobacterial pellets were examined using electron microscopy, and the concentration of monomeric Si in the eluent was determined by the molybdate yellow method described above.

### 2.4. Fe(III) (hydr)oxide-coating cyanobacteria procedure

Homogenized *Calothrix* suspensions were exposed to a low pH ferric nitrate solution containing either 5 or 50 mM Fe(III). The solution was incrementally titrated with small aliquots of 6 M NaOH until the pH of the suspension reached approximately 6, causing precipitation of Fe(III) (hydr)oxide onto the cyanobacterial surfaces (Swelund and Webster, 1999; Fein et al., 2002). The Fe(III) (hydr)oxide-coated cyanobacteria were removed from the precipitating solution via centrifugation and rinsed twice in DDI water and then resuspended in the BG11 + n media. Inorganic Fe(III) (hydr)oxide colloids were also synthesized using the same procedure without the presence of cyanobacteria. XRD analysis of the precipitate indicated that the

Fe(III) (hydr)oxide phase formed was two-line ferrihydrite. Silica precipitation experiments were then conducted with the Fe(III) (hydr)oxide-coated cyanobacteria and inorganic Fe(III) (hydr)oxide colloids following the procedure described in Section 2.2.

## 3. Results

The results show that Si sorption from a 30 ppm Si solution in contact with *Calothrix* was minimal (Fig. 1). In the control experiment, no loss of aqueous Si was observed indicating that precipitation of a solid Si phase and Si sorption onto the experimental apparatus did not occur. In the bacterial experiment, insignificant Si sorption was measured after 24 and 48 h. The presence of cyanobacteria did not remove notable amounts of aqueous Si and changes in Si concentrations were less than the uncertainties of the molybdate yellow analytical technique.

Silica precipitation experiments were conducted with 280 and 70 ppm Si solutions (Fig. 2). At 300 ppm Si, the control experiment showed that the amount of monomeric Si decreases rapidly, and over 50% of the Si polymerizes in less than 8 h (Fig. 2a). Between 8 and 48 h, only small changes in Si concentrations were measured. SAED analysis of the solid precipitate formed after 48 h indicated that the material was noncrystalline. In the bacterial experiment, the rate and extent of Si polymerization was nearly identical to the abiotic control. TEM analysis of the *Calothrix* filaments failed to detect any notable silica mineral formation on the surface of the cyanobacterial filaments.

At lower Si supersaturation states (initial concentration of 70 ppm Si), the amount of monomeric Si remained constant in the control for the duration of the experiment (Fig. 2b). After 48 h, only small changes in molybdate active Si concentration was measured. This observation indicates that monomeric Si was

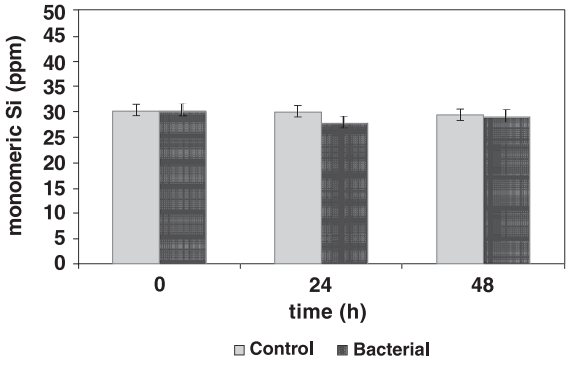


Fig. 1. Si sorption from 30 ppm Si solution at pH 7. The grey columns represent the abiotic control and the black columns represent the bacterial experiment. The error bars represent the analytical uncertainty of the Si measurement. The amount Si sorbed is plotted as concentration of Si remaining in solution.

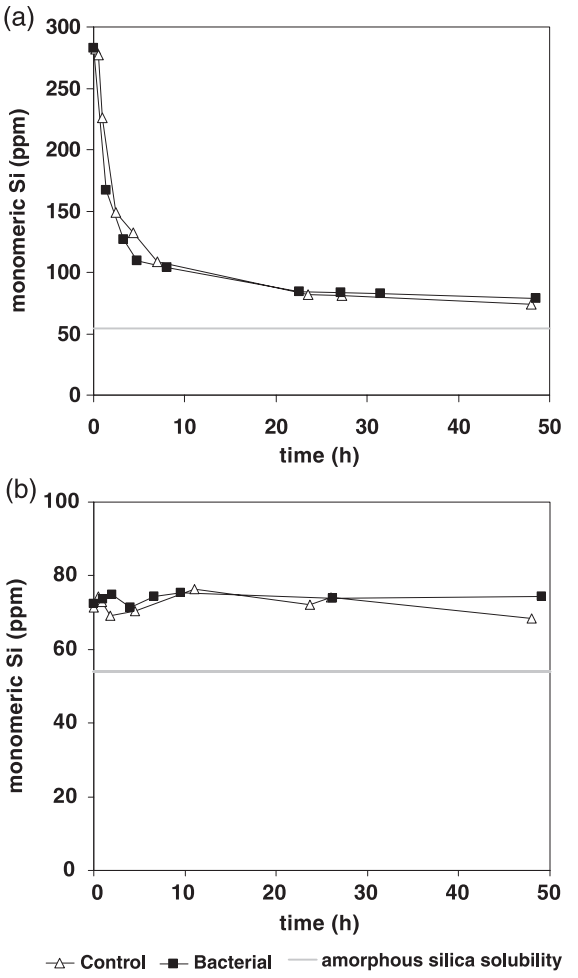


Fig. 2. Silica precipitation by neutralization of an alkaline solution. The open triangles (△) represent the abiotic control, and the solid squares (■) represent the bacterial experiment. The solid grey line indicates the solubility of amorphous silica at 25 °C and 1 bar. Experiments were conducted at pH 7 with initial Si concentrations of (a) 280 ppm, and (b) 70 ppm.

stable and Si polymerization and precipitation had not occurred. In a parallel experiment conducted with *Calothrix*, no notable differences in Si concentrations were observed compared to the control.

Silica precipitation experiments induced by cooling are depicted in Fig. 3. Rapid Si polymerization was observed over the first 5 h due to cooling from 77 to 27 °C in both systems with and without cyanobacteria. In the control experiment, the concentration of monomeric Si decreased from 150 to 70 ppm in 45 h, and the presence of cyanobacteria had a negligible effect on the rate of Si polymerization.

In contrast, silica precipitation experiments conducted with ferrihydrite-coated cyanobacteria indicated that the presence of ferrihydrite surfaces significantly increased the rate and extent of Si removal from solution (Fig. 4). The control experiments without ferrihydrite-coating cyanobacteria showed no significant decrease in Si concentrations indicating that minimal silica precipitation had occurred. However, cyanobacteria coated with 5 mM Fe(III) removed 39% of the Si from solution within 3 h, and gradually removed 89% of the silica in 30 h (Fig. 4a). *Calothrix* filaments coated with 50 mM Fe(III) sorbed 99% of the Si in less than 100 min. Therefore, increasing the amount of ferrihydrite-coating on the cell surface increased the rate and amount of silica sorbed from solution. In experiments performed without the presence of cyanobacteria, the inorganic ferrihydrite colloids display very similar Si removal trends (Fig. 4b). The results show after 26 h that ferrihydrite colloids prepared from 5 mM and 50 mM Fe(III) solutions, sorbed 52% and 99% of the Si. In the 5 mM Fe(III) systems, the inorganic ferrihydrite colloids sorbed less Si than the ferrihydrite-coated cyanobacteria. However, the differences in ferrihydrite surface areas are unknown and difficult to determine for composite microbe–mineral mixtures, thereby limiting direct quantitative comparisons between the two systems.

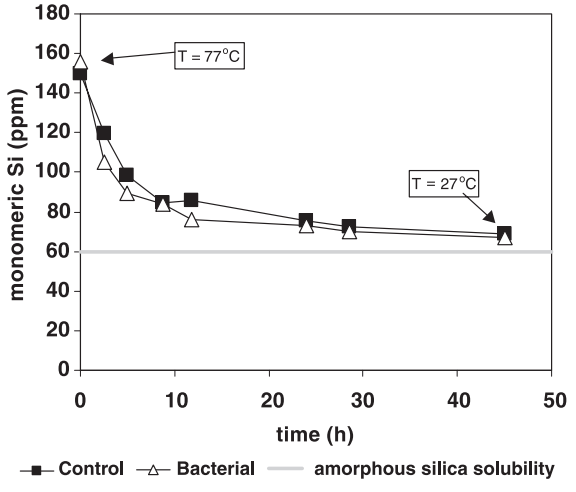


Fig. 3. Silica precipitation by cooling. Initial temperature of 77 °C cooled to 27 °C. The open triangles (△) represent the abiotic control, the solid squares (■) represent the bacterial experiment and the solid grey line indicates the solubility of amorphous silica at 27 °C. Experiments conducted with a 155 ppm Si solution at pH 7.

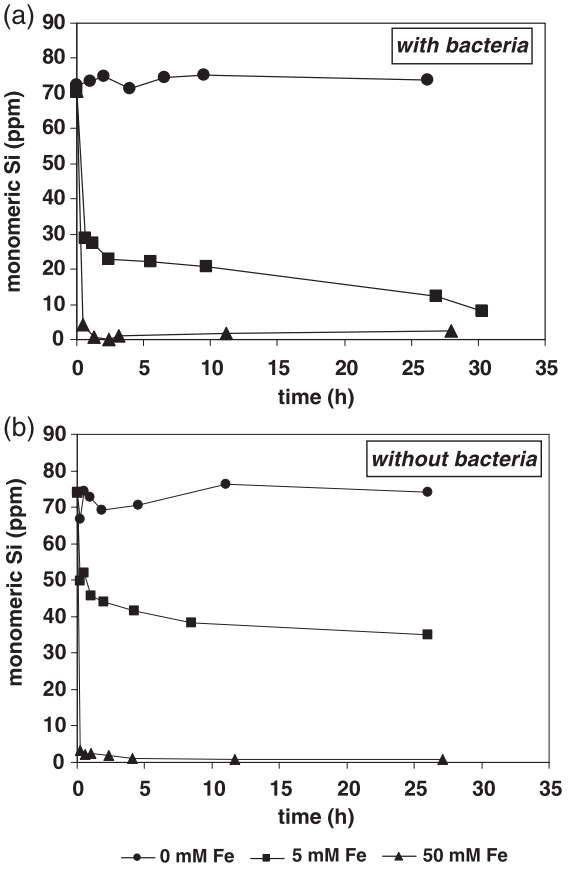


Fig. 4. Si sorption and precipitation onto ferrihydrite-coated cyanobacteria and ferrihydrite colliods. Experiments conducted with a 70 ppm Si solution at pH 7 with (a) ferrihydrite-coated cyanobacteria, and (b) inorganic ferrihydrite colloids without cyanobacteria, prepared from 0 mM (●), 5 mM (■) and 50 mM (▲) ferric nitrate solutions.

## 4. Discussion

Earlier studies have proposed that the microbial-mediated formation of silicate precipitates is caused by Si sorption onto specific bacterial surface sites Urrutia and Beveridge, 1993, 1994, 1995; Fortin and Beveridge, 1997). Recent acid–base titration experiments have revealed that *Calothrix* sp. possess a range of reactive metal-binding sites on both the sheath and cell wall (Phoenix et al., 2002). At neutral pH, the cell surface contains both protonated and deprotonated carboxyl, phosphoryl and amine functional groups. However, the experimental results displayed in Fig. 1 indicate that the interaction between Si and these surface functional groups is weak. In a 30 ppm solution, Si is undersaturated w.r.t. amorphous silica (saturation index, $\Omega = 0.87$) and during the time scale of our experiments, Si is stable as monomeric silica. Under neutral pH conditions, the dominant speciation of monomeric silica is in the form of a neutrally charged complex, $H_4SiO_4$ (Iler, 1979). The results indicate that the stability of a $H_4SiO_4$–*Calothrix* surface complex is very low and cannot be accurately quantified with our experimental approach. This finding is consistent with Fein et al. (2002), who demonstrated that dilute concentrations of aqueous Si do not readily sorb onto the gram-positive bacteria *B. subtilis*.

It has also been proposed that the formation of silicate biominerals is due to microbial enhancement of precipitation kinetics from supersaturated solutions (Schultze-Lam et al., 1995; Konhauser and Ferris, 1996; Konhauser et al., 2001). The presence of microbial surfaces can reduce the activation energy barriers that inhibit nucleation. In supersaturated solutions, the reactive sites on the cell surface can bind and nucleate metals, initiating autocatalytic mineral growth (Warren and Ferris, 1998). In this way, microorganisms provide reactive surfaces facilitating heterogeneous precipitation. However, the data presented in Fig. 2 show that the presence of cyanobacteria has a negligible effect on silica precipitation. In the solution containing 280 ppm Si ($\Omega = 5.14$, w.r.t. amorphous silica), the inorganic polymerization of monomeric Si was rapid and spontaneous. At these high silica supersaturation levels, there is a strong chemical driving force for silica precipitation and homogeneous nucleation is favored. The additional free energy provided by the cyanobacterial surfaces has a negligible effect on the precipitation kinetics. In the solution containing 70 ppm Si ($\Omega = 1.28$, w.r.t. amorphous silica), the degree of supersaturation is lower and the chemical driving force for precipitation is considerably less. At these low Si supersaturation levels, the precipitation of amorphous silica is thermodynamically favored but the reaction kinetics is slow (Rothbaum and Rhode, 1979; Weres et al., 1981). In the presence of cyanobacteria, an enhancement in the reaction kinetics of was not observed. Instead, the data show that the amount of Si in solution remained constant throughout the experiment, suggesting that the presence of microbial surfaces do not promote Si–solid phase nucleation.

The experimental results displayed in Fig. 3 show that silica precipitation from a cooling solution is an inorganic process and further demonstrates the presence of cyanobacteria has a minimal effect on the silica precipitation reaction. A decrease in solution temperature results in Si supersaturation (w.r.t to amorphous silica) and initiates spontaneous Si polymerization. The Si polymerization rates in the bacterial experiment were nearly identical to the inorganic control experiment, suggesting that the presence of microorganisms do not affect the silica precipitation process. The solubility of amorphous silica at 27 °C and 1 bar is approximately $\sim$ 60 ppm, therefore the precipitation reaction was near but had not reached equilibrium. Therefore, under these conditions, the polymerization process is controlled by temperature and time, and there is no evidence that cyanobacterial surfaces nucleate silica mineral formation nor promote silica precipitation by providing additional nucleation sites.

An early study by Walter et al. (1972) proposed that bacterial silicification at hot springs is a passive inorganic process, occurring due to rapid cooling, fluid mixing, evaporation and/or steam loss, and changes in pH of the hydrothermal waters following discharge. Si concentrations in hot springs can reach high levels of Si supersaturation, for example, Octopus Spring, Yellowstone National Park, USA ( $\sim$ 130 ppm Si, Hinman and Lindstrom 1996) and Champagne Pool, Waiotapu, New Zealand (220 ppm Si, Jones et al., 2001). In fluids supersaturated w.r.t, to amorphous silica, hydroxyl groups on the silicic acid molecule combine to form siloxane bonds (Depasse and Watillon, 1970) resulting in the spontaneous

polymerization of monomeric Si to form polymeric Si clusters and three-dimensional nanoparticles 1–2 nm in diameter (Iler, 1979). Previous studies have shown that silica in solutions saturated with respect to amorphous silica occur dominantly as colloids (e.g. Shimada and Tarutani, 1979). Therefore, it is likely that in hydrothermal waters, the inorganic polymerization reaction forms colloidal and polymeric silica which can then deposit onto the microbial cell surface through electrostatic or van der Waals forces (van Loosdrecht et al., 1989). This hypothesis is supported by TEM studies of biomineralization at hot spring environments, which commonly show nanosize siliceous spheres deposited the outer sheath surface of filamentous cyanobacteria (Schultze-Lam et al., 1995; Konhauser and Ferris, 1996; Konhauser et al. 1999; Phoenix et al., 2000).

Earlier studies have also proposed that in the presence of Fe, the role of bacteria in silica and silicate mineralization is to concentrate Fe through sorption/precipitation reactions (Konhauser et al., 1993, 1994; Urrutia and Beveridge, 1994; Fein et al., 2002). In this case, the role of bacterial surfaces in silica mineralization is indirect, and the role of bacteria is to serve as a template for Fe mineral precipitation. The data presented in Fig. 4 demonstrate that ferrihydrite-coated *Calothrix* filaments display a strong affinity for Si and can readily accumulate silica from solution. Monomeric and dimeric silica species can directly bind onto ferrihydrite surface sites and form stable surface complexes (Swelund and Webster, 1999; Davis et al., 2002). Furthermore, at high Si concentrations, ferrihydrite surfaces can act as a template for silica polymerization (Swelund and Webster, 1999). The control experiment illustrated in Fig. 4b indicated that the rate and extent of Si removal can be accounted for by Si partitioning on ferrihydrite surfaces alone. Therefore, it is the ferrihydrite and not the microbial surface which controlled the Si nucleation process.

In geothermal systems, this indirect Si nucleation mechanism may be controlled by the concentration of Fe present in the hot spring fluids. Typical Fe concentrations in hot springs can range from well below 1 ppm, such as Champagne Pool, New Zealand and Strokkur, Iceland (Konhauser and Ferris, 1996; Jones et al., 2001) to Fe levels of 94 ppm, such as at Kamuiwakka Falls, Japan (Asada and Tazaki, 2001). EDS analysis of silicate biominerals from such hot spring environments commonly reveal a significant enrichment in the ratio of Fe–Si in the biomineral compared to the hot spring water (Konhauser and Ferris, 1996). This likely stems from the high affinity between silica and iron (as underlined in this study), thus iron (hydr)oxides are readily incorporated into the amorphous silica matrix. However, there is currently no evidence from field observations that Fe–Si precipitation occurs more rapidly upon bacterial surfaces compared to inorganic surfaces, such as silica sinter. Based upon observations from the current investigation, we hypothesize that iron–silicate biomineralization is an inorganically controlled process and the reaction kinetics are not strongly influenced by the presence of bacteria.

## 5. Conclusions

Field-based investigations have shown that in modern hot spring environments, silica sinters actively form in close spatial relation to microorganisms. However, in this study we demonstrate that aqueous Si displays a low affinity for *Calothrix* sp., and silica nucleation onto cyanobacterial surfaces does not readily occur. These results suggest that in silica supersaturated solutions, microorganisms act as passive surfaces and bacterial silicification is largely controlled by inorganic processes. During ascent to the Earth's surface and upon exposure to atmospheric conditions, geothermal fluid undergo extreme changes in chemical (e.g. redox, pH, saturation state) and physical (e.g. temperature, pressure) properties, and it is these abiotic processes which exert the strongest control on silica precipitation. Although microbial surfaces do not directly nucleate silica mineral formation, they may play an important role in the aggregation of polymeric silica and the deposition of silica colloids. Further investigation is required in order to understand the mechanisms which control colloidal silica–microbe interactions.

## Acknowledgements

This research was funded by the Leverhulme Trust grant number F-00122/F. We would like to thank C. Kennedy with his help on the XRD analysis. **[EO]**

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