**Structure of low-order hemimorphite produced in a Zn-rich environment by cyanobacterium Leptolingbya frigida**

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**ABSTRACT**

Microbes play a fundamental role in the precipitation of silicate biominerals, thereby affecting the Si geochemical cycle. The fine mechanisms ruling biomineralization are not yet fully understood, and their microscopic structures can offer deep insight into their processes of formation, reactivity and stability. In this study, a Zn silicate biomineral, extracellularly produced by cyanobacterium *Leptolingbya frigida*, was investigated combining nuclear magnetic resonance (NMR), Zn K-edge X-ray absorption spectroscopy (XAS) and other complementary techniques. ⁷⁹Si magic angle spinning and ²⁹Si/H cross polarization magic angle spinning analysis, Fourier transform infrared spectroscopy (FTIR) and XAS analysis revealed a poorly crystalline phase closely resembling hemimorphite [Zn₅Si₄O₁₀(OH)₂·H₂O]. Zn K-edge extended X-ray absorption fine structure (EXAFS) provided further structural details, revealing that the Zn-O-Si interatomic distances were 7–8% shorter than the abiotic mineral. ¹³C NMR spectra analysis was conducted to investigate the composition of the Zn silicate biomineral organic matrix, and results revealed that C atoms occurred in several functional groups such as carbonyl carbons, C rings, O-aliphatic chains, N-aliphatic chains, and aliphatic chains.

Under slightly alkaline conditions, bacterial cell walls exhibited fundamental control on the biomineralization process by binding Zn ions and forming Zn–O–Si bonds. In this way, *L. frigida* cell walls served as a reactive surface for the precipitation of this Zn sorosilicate, hindering the condensation of silicon dimers. Moreover, we found a ²⁹Si NMR band at 85 ppm that could be attributed to a (C₅H₄O₃)₂Si complex. This complex could play a role in the control of silicon polymerization, with implications for Si biomineralization processes.

**Keywords:** Zinc, silicon, biomineral, hemimorphite, silicon polymerization, organic Si complexes

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**INTRODUCTION**

In geological history, several kinds of organisms have adopted biosynthesis strategies producing Si biominerals, significantly affecting the Si geochemical cycle (Konhauser 2016). Diatoms and sponges are among the most studied silica biominerals. Diatoms produce their biominerals by polycondensation of Si(OH)₄ (silicic acid) molecules, which occurs in a specific intracellular compartment, termed the silica deposition vesicle (Drum and Pankratz 1964). Sponges (the Porifera) are multicellular (differentiated) sedentary filter-feeder organisms that can produce intracellularly silicified spicules in specialized cells known as sclerocytes (reviewed in Simpson 1984). Other silicifying systems use silica to build biominerals of specific shape and crystal order. Silica and silicates can be found in many higher plants and occur in cell walls, cell lumens, intracellular spaces, roots, leaves, and other spaces (Ma et al. 2001; Neumann and zur Nieden 2001; Valtchev et al. 2003; Ma and Yamaji 2008; Schaller et al. 2013; De Giudici et al. 2014a, 2015; Medas et al. 2015, 2017).

Biosilification mechanisms mediated by bacteria, either involving metal precipitation or not, were extensively investigated in geothermal waters oversaturated with respect to SiO₂aq (Köhler et al. 1994; Fortin et al. 1998; Phoenix et al. 2000). In these systems, silica sinter formation (Benning et al. 2005) is interpreted as a multi-step process: thermodynamically driven polycondensation of silica monomers and the formation of silica nanoparticles first take place, followed by microbially enhanced aggregation of the silica nanostructures into large assemblages. However, little research has been performed on biosilicates precipitated by bacteria from waters undersaturated with SiO₂aq and the control that biopolymers have on Si coordination during biosynthesis is only partially understood. Previous studies pointed out that Fe and/or Al hydroxide-coated cyanobacteria can bind a significant concentration of Si, thereby suggesting that Mg, Fe, and Al play an important role in the formation of silicate biominerals (Urrutia and Beveridge 1993; Konhauser 1998; Konhauser et al. 1993; Fein et al. 2002; Zeyen et al. 2003; De Giudici et al. 2014a, 2015; Medas et al. 2015, 2017).