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

Daniela Medas[1], Carlo Meneghini[2], Francesca Podda[1], Costantino Floris[1], Mariano Casu[1], Maria Antonietta Casu[3], Elodia Musu[4], and Giovanni De Giudici[1,*]

[1]Department of Chemical and Geological Sciences, University of Cagliari, S.S. 554, 09042 Monserrato, Cagliari, Italy
[2]Department of Sciences, University of Roma Tre, Via della Vasca Navale 84, 00146 Rome, Italy
[3]National Research Council, Institute of Translational Pharmacology, UOS of Cagliari, Scientific and Technological Park of Sardinia—POLARIS, 09010 Pula, Cagliari, Italy
[4]CRS4—Microlab Scientific and Technological Park of Sardinia, 09010 Pula, Cagliari, Italy

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. ^{29}Si magic angle spinning and ^{29}Si/^{1}H cross polarization magic angle spinning analysis, Fourier transform infrared spectroscopy (FTIR) and XAS analysis revealed a poorly crystalline phase closely resembling hemimorphite [$Zn_4Si_2O_7(OH)_2 \cdot H_2O$]. 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. ^{13}C 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 ^{29}Si NMR band at 85 ppm that could be attributed to a $(C_3H_6O_3)_2Si$ 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