

Mechanism and crystallochemical signature of nano-particle formation by microorganisms

H. SHIOTSU¹, M. JIANG¹, Y. NAKAMATSU¹, T. OHNUKI²
AND S. UTSUNOMIYA¹

¹Department of Chemistry, Kyushu University, Fukuoka 812-8581, Japan (utsunomiya.satoshi.998@m.kyushu-u.ac.jp)

²ASRC, Japan Atomic Energy Agency, Tokai, Ibaraki, Japan

Interaction between rare earth elements (REEs) and microorganisms have attracted increasing attention due to the ubiquitous occurrence of microorganisms in the subsurface environment and to implication to the safety assessment of nuclear waste disposal, as REEs are used as a surrogate of trivalent actinides. Post-adsorption nano-mineralization by microorganisms is a key process that can constrain the migration of REEs; however, the mechanisms and factors controlling the process are still unclear. This study demonstrates the REEs (La-Lu) accumulation experiments to understand the effect of pH, coexistent REEs and the functional group of cells surfaces on the crystal chemistry of biogenic nanoparticle formation.

During the exposure of yeast to REE solution at 25 °C, all REEs were removed from the solution by 24 h at pH 4 and 5, while 50 % of the initial amount remained in the solution at pH 3 after 24 h. Deprotonation of the functional groups on the cell surface merely occurs at pH 3 as evidenced by the other experiments at 4 °C. In contrast, 10 % of REEs were adsorbed to the cell surfaces at pH 4 and 5. Particles at the size of ~100 nm precipitated on the cell surfaces at pH 3, while ~30 nm-sized nano-particles were observed at pH 4 and 5 at 25 °C. These nano-particles were characterized as phosphate containing a series of REEs. The nano-particles at pH 3 had monazite structure, while the particles forming at pH 4 and 5 were amorphous, indicating that crystallization took place only at pH 3. REE phosphate inorganically synthesized at room temperature revealed crystalline structure (monazite, xenotime or rhabdophane) depending on the element. Additional inorganic model experiments using the CMC, Ln resin and Cellulose Phosphate, which have the functional groups similar to cell surfaces, demonstrated that the nano-particles precipitated without structure. Based on these data it is suggested that adsorption to the functional groups on the cell surfaces constrain the shape and structure of nanoparticles.

As for the REE pattern, the difference between the distribution coefficient, K_d (ml/g), of LREE and of HREE increased with time increasing. At 24 h, the K_d ratio of Nd to Tm ($K_{d, Nd}/K_{d, Tm}$) is 1.72, 4.61, and 6.86 at pH 3, 4, and 5, respectively. The K_d ratios greater than 1 indicate the preferential uptake of LREE by the microorganisms, which are attributed to the lower solubility products of REE phosphate. As a consequence, the present study underscores the important role of cell surfaces and biological activity on the kinetics, mechanisms and crystal chemistry of nanoparticle formation as well as the physico-chemical properties of nanoparticles.

Sub-daily elemental fluctuation in mussel shell

KOTARO SHIRAI^{1*}, TSUZUMI MIYAJI², BERND R. SCHÖNE³ AND KAZUSHIGE TANABE⁴

¹Atmosphere and Ocean Research Institute, The University of Tokyo, Kashiwa 277-8564 Japan (* correspondence: kshirai@aori.u-tokyo.ac.jp)

²Department of Natural History of Science, Hokkaido University, Sapporo 060-0810 Japan

³Institute of Geoscience, University of Mainz 55128 Mainz Germany

⁴The University Museum, The University of Tokyo, Tokyo 133-0033 Japan

Shells of bivalve mollusks such as mytiloids serve as excellent paleoenvironmental archives. They exhibit a broad biogeographic distribution, occur in large numbers in the fossil record and contain a temporally aligned and highly resolved record of past environmental parameters. For example, Mg/Ca ratios of mussel shells have been explored as a temperature proxy. According to several studies, however, the suitability of the Mg/Ca thermometer is limited by vital effects. In order to extract reliable environmental information from the shell through geochemical analyses it is essential to understand the mechanism of elemental incorporation into the shell during calcification and growth.

In the present study, we have analyzed Mg/Ca Sr/Ca and S/Ca ratios of two shells of the Mediterranean mussel *Mytilus galloprovincialis* collected alive from Tokyo Bay, Japan. Environmental parameters were monitored at the sampling site. The elemental distribution was determined in polished cross-sections by means of electron probe micro analysis. Growth patterns were used to place the geochemical data in a temporal context.

Growth lines (which formed during low tide) showed higher Mg/Ca ratios compared to adjacent growth increments. S/Ca ratios were also high at the growth line. However, the Mg/Ca and S/Ca do not show linear correlation. Both Mg/Ca and S/Ca ratios showed significant periodic fluctuations at the sub-seasonal scale. These fluctuations likely indicate that the shell Mg/Ca ratios primarily reflect biological changes caused by tidal cycle and do not record temperature.