

Detection of Sr and Ca Stable Isotope Fractionation during CaCO₃ Formation from Seawater to Investigate the Mechanism of Biomineralization

Tomoko Ariga¹, Michio Suzuki², Gen Shimoda³

¹ National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), ² Department of Applied Biological Chemistry, The University of Tokyo,

³ Geological Survey of Japan (GSJ), National Institute of Advanced Industrial Science and Technology (AIST)

Summary

Marine organisms such as shellfish, sea urchins, and corals efficiently fix calcium ions (Ca²⁺) in seawater as calcium carbonate (CaCO₃) through biomineralization. In this process, species-specific proteins called biomineralization proteins control the crystal polymorphism of CaCO₃. Although controlling the polymorphism of CaCO₃ crystals using biomineralization proteins may lead to the development of a low-cost and highly efficient technology for fixing atmospheric CO₂ as CaCO₃ using Ca in seawater, the mechanism of controlling CaCO₃ crystal polymorphism by biomineralization proteins has not been elucidated. This study aimed to investigate the function of biomineralization proteins by detecting Sr and Ca stable isotope fractionation that occurs during CaCO₃ crystals formation through biomineralization process by several kinds of shellfish and artificially reproduced biomineralization reaction system or in.

Since the magnitude of stable isotope fractionation of Sr and Ca that occurs during CaCO₃ crystal formation is minute, a highly precise and accurate technique for measuring Sr and Ca stable isotope ratios (⁸⁸Sr/⁸⁶Sr and ⁴⁴Ca/⁴²Ca) is essential. Firstly, the following techniques to achieve precise and accurate ⁸⁸Sr/⁸⁶Sr measurement were developed. (1) effective Sr/matrix separation method using Sr resin: to achieve precise and accurate ⁸⁸Sr/⁸⁶Sr measurement using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), highly effective Sr/matrix separation prior to the measurements is essential. In this study, Sr/matrix separation procedure using Sr resin was optimized, resulting in good Sr/matrix separation and high Sr recovery (97 %). (2) Highly sensitive ⁸⁸Sr/⁸⁶Sr measurement method using MC-ICP-MS: since the amount of synthetic CaCO₃ crystals obtained from the artificial biomineralization reaction is extremely small, improvement of the sensitivity of ⁸⁸Sr/⁸⁶Sr measurement using MC-ICP-MS was carried out, resulting in a four-fold increase in sensitivity compared to the conventional method. Finally, the optimized Sr/matrix separation procedure was applied to the synthetic CaCO₃ crystals and shell samples, and effective Sr/matrix separation was achieved.