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Biological controls on Sr/Ca, Ba/Ca and Carbon isotope in freshwater pearl mussel *Hyriopsis* sp.

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Biogenic skeletons of marine and freshwater organisms are important archives of paleoenvironmental information. Bivalves occur in various environments from polar region to low latitude region, in freshwater and marine, and have carbonate shells which are formed by addition growth. So they have the potential to contain the paleoenvironmental information within their isotope and elemental compositions. Freshwater environment sensitively reacts to the climate changes and is well known as a role of the material transportation from continental regions to seawater following chemical and physical weathering. So freshwater bivalves gather much attention as time-series paleoenvironmental archives. By this time, there are many reports on elemental and isotope fractionation of marine bivalves, but little is known about freshwater bivalves.

In this study, we analyzed the trace element (Sr/Ca and Ba/Ca) and stable isotope (oxygen and carbon) ratios of a commercially cultured freshwater pearl mussel *Hyriopsis* sp. shells (*Bivalvia Unionidae*) and ambient water in Lake Kasumigaura. Our aim was to assess what is the factors influencing Sr/Ca, Ba/Ca, and carbon isotope ($d^{13}C_{SHELL}$) ratios freshwater bivalve shells.

Element ratios (Sr/Ca and Ba/Ca) in the three shell specimens were measured with a quadrupole ICP-MS and stable isotope ratios ($d^{18}O_{SHELL}$ and $d^{13}C_{SHELL}$) with an isotope ratio mass spectrometer. Shell structures were observed by the microscope and by inspection of the external shell. Trace element ratios (Sr/Ca and Ba/Ca) of water samples were calculated from the Ca, Sr and Ba concentrations, which were measured with an ICP-AES. $d^{13}C_{DIC}$ was measured by isotope ratio mass spectrometer. We compare the element/isotopic profiles of shells among various parameters such as water temperature, annual growth rate, and elemental/carbon isotope ratios of ambient water.

Sr/Ca ratios of water remained relatively constant throughout years. Clear annual Sr/Ca cycles of shell suggest that Sr was incorporated into the shells at a high rate during warm seasons. If the Sr incorporation is governed by thermodynamic control, Sr/Ca profiles show a negative correlation with ambient temperature. However, between Sr/Ca and $d^{18}O$ profiles negative correlation is found. That indicates primary controlling factor of a Sr incorporation into *Hyriopsis* shell is not thermodynamic partition. All three examined shells showed a clear decrease in annual average Sr/Ca with age. Inter- and intra-annual trends suggest that Sr incorporation was higher during periods of faster growth.

The Ba concentration and the Ba/Ca ratio of ambient water showed neither an annual periodicity nor a seasonal trend. In contrast to the findings of an inorganic aragonite precipitation experiment, Ba/Ca was positively correlated with ambient temperature. In addition, Ba/Ca and Sr/Ca ratios were positively correlated with each other. These results suggest that not thermodynamic equilibrium partitioning but the shell growth rate controls Ba incorporation into *Hyriopsis* shells.

The $d^{13}C_{DIC}$ showed a wide range fluctuation from -14.63 to -8.62 per mill. The enrichment of $d^{13}C$ was observed in summer samples. On the other hand, the $d^{13}C_{SHELL}$ varied mainly from -12 to -9 per mill and its pattern was not symmetric and sinusoidal like the water temperature profile. A carbon isotopic mixing equation presented by McConnaughey et al. [1997] describes the combination of respired and environmental carbon incorporated into the precipitating carbonate. The calculated values of $d^{13}C_{SHELL}$ under equilibrate with $d^{13}C_{DIC}$ are ranged from -11.93 to -9.41 per mill and are consistent with observed shell data. Thus, the primary factor controlling the value of $d^{13}C_{SHELL}$ is not the respired effects but the carbon isotope fluctuations of ambient DIC.

*McConnaughey, T. A., J. Burdett, J. F. Whelan, and K. P. Charles (1997), *Cosmochim. Acta*, 61, 611-622.

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