

Effects of carbonate chemistry and metabolism induced by ocean acidification on stable isotope fractionation in molluscan shell carbonate

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Stable oxygen and carbon isotope compositions of biogenic carbonate have been widely used for many paleoclimate, paleoecological, and biomineralization studies. Oxygen isotope compositions of carbonate, a commonly used proxy of seawater temperature and oxygen isotope compositions of seawater, are also affected by seawater carbonate chemistry, but the knowledge of its dependency on stable isotope fractionation of both synthetic and biogenic aragonite is still limited. It has also been reported that carbon isotope compositions of molluscan shells are affected by carbon isotope compositions of seawater carbonate chemistry and metabolic carbon. Several studies reported effects of ocean acidification on metabolism of molluscs, and thus the metabolic changes could potentially influence the stable isotope compositions of metabolic carbon. Here, we have focused on stable oxygen and carbon isotopic responses of molluscan shells to CO₂-driven seawater acidification for understanding of the contribution of environmental and metabolic effects. Two species of clams (*Scapharca broughtonii*, *Pseudocardium sachalinense*) and two species of abalones (*Haliotis discus discus*, *Haliotis gigantea*) were cultured in seawater chemically manipulated to vary pCO₂ condition using CO₂ control system of the Demonstration Laboratory, Marine Ecology Research Institute (MERI), in Kashiwazaki City, Niigata Prefecture, Japan.

Stable oxygen isotope compositions of *S. broughtonii* had significant negative correlations with pH (-0.48‰ /pH, at 17°C; -0.61‰ / pH, at 25 °C). These of *P. sachalinense*, *H. discus discus*, and *H. gigantea* showed non-significant relationships with pH and small variations (within 1 per mil). The oxygen isotope fractionation in four species of our study are smaller than that of synthetic calcite (-1.42‰ / pH, Zeebe et al., 1999).

The significant negative correlations between stable carbon isotope compositions and pH appeared in *S. broughtonii*, *H. discus discus*, and *H. gigantea* which had non-significant pH effects on calcification, and the slopes of these relationships of shell carbonate were lower than these of dissolved inorganic carbon (DIC) of seawater. We estimated the equilibrium values of carbon isotope compositions at each pCO₂ treatment, and the difference between the carbon isotope compositions of shell carbonate and equilibrium values showed gradual increases of carbon isotope values with decreasing pH in *S. broughtonii*, *H. discus discus*, and *H. gigantea*. Thus, the pCO₂-induced change in metabolism might appear in carbon isotopes of shells of these species as the metabolic effect. On the other hand, in *P. sachalinense* which showed a decrease in calcification in our culture experiment of ocean acidification, the difference between the carbon isotope compositions of shell carbonate and equilibrium values did not indicate a significant pH dependency. This result might be attributable to differences in metabolic responses to acidified seawater.

The findings of our study will contribute to the correction of isotopic paleotemperature of biogenic carbonate and the understanding of acidification effects on metabolism of marine calcifiers.

Keywords: ocean acidification, stable isotopes, mollusca, biomineralization, proxy, pH