

Evaluation of carbon and oxygen isotopic compositions of brachiopod shells as paleoenvironmental indicators

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Carbon and oxygen isotopes in biogenic carbonates are powerful tools for paleoenvironmental analysis. The isotopic compositions of brachiopod shell have been regarded as an excellent environmental proxy based on the two reasons:

1) Low Mg calcite shells of brachiopods are subject to less diagenetic alteration than aragonitic skeletons of other marine invertebrates; and

2) It was shown that brachiopod shells are precipitated in isotopic equilibrium with ambient seawater (Lowenstam, 1961).

Recent investigations, however, revealed that some criteria which have been commonly used to evaluate the preservation state of brachiopod shells are not inappropriate and that brachiopod shells are not necessarily precipitated in isotopic equilibrium with ambient seawater (Auclair et al., 2003).

In order to clarify to what extent original isotopic compositions of brachiopod shells are modified due to varying degrees of diagenetic alteration, we conducted geochemical and paleontological studies on fossil and living *Kikaithyris hanzawai* (Yabe).

The dead brachiopods were collected at depth of 180 m off Amami-o-shima in September 1993. Annual bottom seawater temperature ranges from ~18 to ~22 degrees centigrade at this site. Samples for isotopic analysis were collected at a particular portion in the fibrous secondary shell layer to minimize the vital effect on carbonate precipitation which varies with the shell growth rate. Our analysis showed that $\delta^{18}\text{O}$ values of the secondary layer of *K. hanzawai* are greater by ~1.5 permil than those of the inorganic carbonate precipitated in isotopic equilibrium with ambient seawater.

We measured isotopic compositions of fossil *K. hanzawai* collected from Pleistocene carbonates on Kikai-jima (0.08 Ma) and Nakijin, Okinawa-jima (0.41-1.65 Ma). The fossil *K. hanzawai* occurred from shelf carbonates, where the paleoceanographic conditions were similar to those of the site off Amami-o-shima. A total of 64 shells were analyzed. Samples for isotopic analysis were taken from the same portion as those from the modern shells. We estimated $\delta^{18}\text{O}$ values of the seawater when the brachiopods lived based on the composite $\delta^{18}\text{O}$ curve (Williams et al., 1988) and calculated presumed original $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the fossil brachiopod shells. Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the fossil shells were less than the presumed values. This implies that the original isotopic compositions have been modified due to meteoric diagenesis.

We quantified degrees of the preservation state of shell microstructures by calculating a ratio (percent) of altered fiber area and a ratio (percent) of luminescent area both in the transverse section. No significant relationships were recognized between isotopic compositions and these ratios.

Our study does not indicate general rejection of availability of isotopic compositions of brachiopod shells as paleoenvironmental proxies. Further geochemical investigations are needed on isotopic compositions of brachiopod shells and their modification due to diagenetic alteration.