## Evaluation of carbon and oxygen isotopic compositions of modern brachiopod shells as paleoenvironmental proxies

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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 [1].

Recent investigations, however, revealed that brachiopod shells are not necessarily precipitated in isotopic equilibrium with ambient seawater [2].

This study presents carbon and oxygen isotopic compositions of shells of five modern brachiopod species (*Terebratulina crossei*, *Terebratalia coreanica*, *Laqueus rubellus*, *Kikaithyris hanzawai*, and *Basiliola lucida*) which lived in cool, warm-temperate, and subtropical sites in Japan. High-resolution, three-dimensional samplings were conducted (1) to clarify variations in the isotopic compositions in a single shell and within and between species, (2) to evaluate offset of the compositions from those of the calcite precipitated in isotopic equilibrium with ambient seawater (equilibrium calcite), and (3) to specify species and shell portions that reflect the isotopic compositions of ambient seawater.

d18O values of samples from the secondary shell layer that constitutes the main body of a brachiopod shell are in and/or out of those of the equilibrium calcite. The greater and smaller d18O values of samples from brachiopod shells than those of the equilibrium calcite would cause significant over- and underestimations of seawater temperature. The shell isotopic compositions are correlated well with growth rates. However, the extent of 18O disequilibrium largely depends on species.

Positive correlations between the d13C and d18O values of samples from the outermost part of the secondary shell layer are ascribed to kinetic fractionation effects. However, isotopic compositions of the samples from low growth-rate portions in the secondary layer are often enriched only in 18O than those of equilibrium calcite. Metabolic influences are identified in the isotopic compositions of the samples from the innermost part of the secondary layer of *T. crossei*, *T. coreanica*, and *L. rubellus*, resulting in decreases in the d13C values although the d18O values are not affected.

d18O values of samples from the 'early stages' in the ontogenetic series (uppermost parts of the secondary layers along 'ontogenetic' transects parallel to growth axes of shells) of *T. crossei* and *T. coreanica*, and those from the ontogenetic series of *L. rubellus* would be the most reliable environmental proxies, because they fall in or are close to ranges of those of the equilibrium calcite. Minor intraspecific variations in isotopic compositions of such shell portions would enable us to decipher secular isotopic fluctuations at relatively high resolution less than 0.5 per mill.

This study clearly illustrates that the carbon and oxygen isotopic compositions of the modern brachiopod shells are predominantly influenced by kinetic fractionation and, to a lesser extent, by metabolic effects. However, appropriate selection of species and shell portions that reflect the isotopic composition of ambient seawater makes it possible to reconstruct secular variations in d13C or d18O in the past oceans and provide seasonal environmental records for several years.

## References

[1] Lowenstam, H. A., 1961. Jour. Geol., 69, 241-260.

[2] Auclair, A., Joachimski, M. M. and Lecuyer, C., 2003. Chem. Geol., 202, 59-78.