

Evaluation of early diagenetic influence on nitrogen isotopes within fossil amino acids: Towards estimation of ancient food webs

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Compound-specific isotope analysis (CSIA) of nitrogen within amino acids is a relatively new tool to estimate the trophic level of organisms (Chikaraishi et al. 2009; Limnol Oceanogr Meth). It would be applicable as a new technique to the trophic and ecological study of fossils. Hard parts (e.g. shells and bones) usually contain amino acids, which can be extracted and identified in a number of previous studies. However, amino acids in fossils would be influenced by diagenesis, including thermal maturation, racemization, and degradation. Thus, it is important to evaluate whether or not the amino acids within the shell keep the original isotopic composition of organisms. Thus, this study aim to evaluate consistency of the estimated trophic level based on the CSIA of amino acids in shells with respect to early diagenesis. We use modern and fossil *Turbo cornutus* (Gastropoda), which is presumably primary consumer, i.e. trophic level should be 2.0. Fossil *Turbo* were obtained from Yuigahama archaeological site (Kanagawa Pref., Kamakura Era, 13-14th century, ca. 800 years ago) and Torihama archaeological site (Fukui Pref., Jyomon Era, ca. 4000 years ago). The modern materials were obtained from Hakui, Ishikawa and Kaneda, Chiba. Some of the modern materials were heated at 200 and 400 °C in oven.

Prior to the isotope analysis, the samples were examined in several ways, including X-ray diffraction pattern analysis, SEM observations of shell microstructures, D/L ratio of amino acids within the shells to evaluate the preservation of the samples. *Turbo cornutus* shell was composed of three layers. Our observation reveal that the outer layer of the shell contaminated by encrusting biota. Middle layer, consists of nacreous structure, sometimes had erosion by microbes. Moreover, microstructures of the modern sample heated at 400 °C were partially dissolved and recrystallized, and no amino acid was found in there. Amino acid composition in these aged samples was similar to the clean modern ones. Based on those results, we used several fossil samples, which remained original microstructures, for the isotope analysis. We also analyzed modern samples, including those heated at 200 °C and invaded by microbes.

As a result, all the samples analyzed show around 1.9-2.3 for the trophic level estimated based on the CSIA of amino acids. It is indicated that the early diagenesis wouldn't affect to the nitrogen isotopes of amino acids in shells at least for 4000 years.

Keywords: Trophic level, fossil, amino acids, stable nitrogen isotope ratios, early diagenesis