

## Supplement

貝類の炭素・酸素安定同位体比研究——生物源炭酸塩を活用した古生物研究への応用に向けて. 西田 梢, 2020. 化石, (107), 5–20.

西田 梢\*\*\*

\*茨城工業高等専門学校国際創造工学科・\*\*独立行政法人日本学術振興会

**Stable carbon and oxygen isotopes of molluscan shells: Implications to paleontological studies on biological carbonates. Kozue Nishida, 2020. Fossils, 107, 5–20.**

Kozue Nishida\*\*\*

\*Department of Chemistry and Material Engineering, National Institute of Technology, Ibaraki College, Hitachinaka, Ibaraki 312-8508, Japan (nishida@gm.ibaraki-ct.ac.jp); \*\*Japan Society for the Promotion of Science (JSPS), Kojimachi Business Center Building, Chiyoda-ku, Tokyo 102-0083, Japan

図および表の日本語・英語キャプション

**Japanese and English Captions of Figures and Table.**

図1 無機合成および生物源炭酸塩の酸素同位体比と水温の関係. (1) 無機合成アラゴナイト (Kim *et al.*, 2007); (2) 無機合成カルサイト (Watkins *et al.*, 2014); (3) 無機合成カルサイト (Kim and O'Neil, 1997), 魚類耳石 (4)–(8) [(4) Radtke *et al.*, 1996; (5) Thorrold *et al.*, 1997; (6) Patterson *et al.*, 1993; (7) Sakamoto *et al.*, 2017; (8) Kitagawa *et al.*, 2013], (9) 貝類および有孔虫殻 (Grossman and Ku, 1986); 二枚貝殻 (10)–(13) [(10) Owen *et al.*, 2008; (11) Watanabe and Oba, 1999; (12) Aharon and Chappell, 1983; (13) Nishida *et al.*, 2015]; サンゴ骨格 (14)–(19) [(14) Nishida *et al.*, 2014a; (15) Jullet-Leclerc *et al.*, 1997; (16) Leder *et al.*, 1996; (17) Hirabayashi *et al.*, 2013; (18) Wellington *et al.*, 1996; (19) Nishida *et al.*, 2014b]. Kim *et al.* (2007)に従い, 無機合成アラゴナイトの同位体値 (Kim *et al.*, 2007) は, カルサイトのリン酸反応の同位体分別係数 1.01025 (Sharma and Clayton, 1965) で再計算を行った.

Fig. 1. Oxygen isotope fractionation between synthetic and biological carbonates and water as a function of temperature.  $1000 \ln \alpha$  data are shown for (1) *in vitro* aragonite (Kim *et al.*, 2007); (2) *in vitro* calcite (Watkins *et al.*, 2014); (3) *in vitro* calcite (Kim and O'Neil, 1997); aragonite fish otoliths (4)–(8) [(4) Radtke *et al.*, 1996; (5) Thorrold *et al.*, 1997; (6) Patterson *et al.*, 1993; (7) Sakamoto *et al.*, 2017; (8) Kitagawa *et al.*, 2013]; (9) aragonite molluscan and foraminiferal shells (Grossman and Ku, 1986); aragonite bivalve shells (10)–(13) [(10) Owen *et al.*, 2008; (11) Watanabe and Oba, 1999; (12) Aharon and Chappell, 1983; (13) Nishida *et al.*, 2015]; aragonite coral skeletons (14)–(19) [(14) Nishida *et al.*, 2014a; (15) Jullet-Leclerc *et al.*, 1997; (16) Leder *et al.*, 1996; (17) Hirabayashi *et al.*, 2013; (18) Wellington *et al.*, 1996; (19) Nishida *et al.*, 2014b]. The aragonite–water fractionation factor ( $1000 \ln \alpha$ ) of Kim *et al.* (2007) was recalculated using a calcite acid fractionation factor of 1.01025 (Sharma and Clayton, 1965).

図2 貝殻・軟体部の断面図とカルシウム・溶存無機炭素の移動経路。殻・軟体部および殻皮で囲まれた閉鎖空間の石灰化スペースには、外套膜外液 (EPF) が満たされている。炭酸脱水酵素 (CA) とカルシウム ATPアーゼは、貝類の溶存無機炭素のイオン組成を制御する役割をもつ。

Fig. 2. Schematic illustrations of a cross section of a bivalve shell and associated soft tissue and a model of the transport route of calcium and dissolved inorganic carbon (DIC). The calcification site in a mollusc (known as the extrapallial space) is a closed space filled with extrapallial fluid (EPF) surrounded by shell, mantle tissue, and periostracum. The activities of two enzymes (carbonic anhydrase (CA) and  $\text{Ca}^{2+}$  ATPase) play an important role in regulation of the carbonate chemistry of molluscs (McConnaughey and Gillikin, 2008; Le Roy *et al.*, 2014; Spalding *et al.*, 2017).

図3 A: 溶存無機炭素 (二酸化炭素, 炭酸, 炭酸水素イオン, 炭酸イオン) の濃度と pH の関係 (Sade and Halevy, 2017)。全炭酸のモル濃度 15 mM, 25°Cの淡水条件。B: 溶液内での溶存無機炭素の各イオンの反応の割合 (Sade and Halevy, 2017)。それぞれの反応の占める割合は DIC 濃度や各イオンの割合に規制されている。CO<sub>2</sub>の水和化の割合は、pH が低下すると増加する。

Fig. 3. A: Equilibrium concentrations of dissolved carbonate species (DIC) as a function of pH: CO<sub>2</sub> (aq.), H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>, showing the mole fractions of 15 mM DIC in equilibrium at 25 °C under fresh water conditions. B: Equilibrium fluxes in the DIC system. This figure is reprinted from Sade and Halevy (2017). The magnitudes of the fluxes are controlled by DIC concentration and speciation; the flux of CO<sub>2</sub> hydration likely increases with decreasing pH.

表1 貝類の石灰化における呼吸由来の溶存無機炭素 (DIC) および海水の DIC の寄与率 (%)。

Table 1. Percentage contributions of metabolic carbon and inorganic carbon dissolved in seawater (DIC) to molluscan shell formation reported by previous studies.