

NanoSIMS analyses of Mediterranean mussel shells

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For the purpose of paleoceanographic study, we have developed a method to measure minor and trace elements concentrations of natural calcium carbonates using a NanoSIMS [1] and applied to foraminiferal tests [2], branching coral skeleton [3], and giant clam shells [4] [5]. In this study we measured Mediterranean mussel (*Mytilus galloprovincialis*) collected at the Otsuchi bay, on the Pacific coast of northeastern Japan. This bivalve was living at intertidal zone and collected on September 6th 2011, that should have experienced a great tsunami induced by the 2011 magnitude 9.0 Tohoku-Oki earthquake on March 11th.

In the laboratory, soft tissues were removed from mussel and the shell was cut along the maximum growth axis and mounted in Araldite disk together with a carbonate standard. After polishing and gold coated, we analyzed Mg/Ca, Sr/Ca and Ba/Ca ratios of two individual shells by low resolution (10-micron spot at 100-micron interval) and high resolution (2-micron spot at 3-micron interval) along the growth axis. Age-model was facilitated by counting the etched-stained lines using “Mutvei's solution”.

Annual variations of Mg/Ca ratio, high in summer and low in winter, are clearly visible at low resolution of both samples. This may reflect the seawater temperature control [6]. Sr/Ca ratio of one sample shows annual change harmonic with Mg/Ca, while the other unilateral increase. Ba/Ca ratios are constant before the tsunami and significantly variable after that. High resolution analysis of Mg/Ca ratios at non-tsunami part indicates daily or bidaily cyclic changes, which may reflect tidal oscillation. Ba/Ca ratio of high resolution mode is more variable after the tsunami than the before, suggesting larger terrigenous contribution into the shell [7].

[1] Sano et al. (2005) *Anal. Sci.* **21**, 1091. [2] Kunioka et al. (2006) *G-cubed* **7**, Q12P20. [3] Shirai et al. (2008) *Geochim. Comoschim. Acta* **72**, 5386. [4] Sano et al. (2012) *Nature Commu.* **3**, 761. [5] Hori et al. (2015) *Sci. Rep.* **5**, 8734. [6] Wanamaker et al., (2008) *Geo-Mar Lett.* **28**, 359. [7] Gillikin et al. (2006) *Geochim. Comoschim. Acta* **70**, 395.