

High-resolution ontogenic distribution of Mg/Ca ratios and Mg isotopes in modern brachiopods

JURAJ FARKAŠ^{1*}, ADAM TOMAŠOVÝCH², VLADISLAV CHRASTNÝ¹, DORRIT JACOB³, MICHAELA FRANCOVÁ⁴, FLORIAN BÖHM⁵ AND HAUKE VOLLSTAEDT⁵

¹Czech Geological Survey, Prague, Czech Republic, juraj.farkas@geology.cz (* presenting author)

²University of Chicago, Chicago, USA, tomasovych@uchicago.edu

³Johannes Gutenberg-Uni., Mainz, Germany, jacobd@uni-mainz.de

⁴Charles University, Prague, Czech Republic, francova@geology.cz

⁵Geomar | Helmholtz Centre for Ocean Research, Kiel, Germany.

Shells of articulate brachiopods composed of low-Mg calcite provide valuable archives of temporal changes in trace element and isotope composition of past ocean water [1, 2]. However, in order to faithfully reconstruct the paleo-seawater signatures from geochemical data encoded in fossil brachiopods, one must have a full understanding of trace element incorporation, and the accompanying isotope fractionation during shell formation, in modern brachiopod species. Here we present high-resolution ontogenetic profiles of trace element distribution (i.e. Mg/Ca ratios) and Mg isotope variation ($\delta^{26/24}\text{Mg}$) in species of modern articulate brachiopods, *Terebratalia transversa* and *Terebratella sanguinea*, collected from the northeast (San Juan Island, Friday Harbor) and the southwest Pacific Ocean (New Zealand, Doubtful Sound), respectively. Results from LA-ICP-MS (Agilent 7500ce) and wet chemistry (Thermo X-Series II) elemental analysis indicate that Mg/Ca ratios (mmol/mol) in the secondary-layer composed of low-Mg calcite range between 5 and 10, whereas a thin primary layer composed of high-Mg calcite yielded significantly higher Mg/Ca ranging from 25 up to 50. Results of the isotope analysis, done on MC-ICP-MS (Thermo Neptune), show that for low-Mg calcite of modern brachiopods there is no significant species-dependent fractionation of stable Mg isotopes, as $\delta^{26/24}\text{Mg}$ (DSM3) signatures of secondary shell layers of *T. transversa* and *T. sanguinea* yielded identical values of -2.225 ± 0.055 and -2.241 ± 0.187 per mil, respectively. Moreover, these values are also identical with those from modern *Terebratulina retusa* with published $\delta^{26/24}\text{Mg}$ signatures of -2.075 ± 0.097 [3] and -2.290 ± 0.060 [4]. Hence, our preliminary data seem to support an existence of a common taxon-specific control of Mg isotope fractionation during biocalcification of low-Mg calcite of brachiopod shells from ambient seawater. In addition, we found no resolvable temperature-dependent Mg isotope fractionation for samples representing habitat temperatures ranging from 8.8 to 13.7 °C. However, a single sample with an estimated 8 to 15% contribution of Mg from primary high-Mg calcite layer (calculated based on Mg/Ca mass-balance) yielded significantly lower $\delta^{26/24}\text{Mg}$ of -2.819 ± 0.099 , suggesting that an extra caution has to be exercised during sampling of brachiopod shell material for $\delta^{26/24}\text{Mg}$ analysis. We plan to present new Mg/Ca and $\delta^{26/24}\text{Mg}$ data from several other modern brachiopod species, and discuss their implications for paleo-seawater $\delta^{26/24}\text{Mg}$ reconstructions.

[1] Lee et al. (2004) *Chemical Geology* **209**, 49-65. [2] Veizer et al. (1999) *Chemical Geology* **161**, 59-88. [3] Wombacher et al. (2011) *Geochimica et Cosmochimica Acta*, **75**, 5797-5818. [4] Hippler et al. (2009) *Geochimica et Cosmochimica Acta*, **73**, 6134-6146.

Boron isotopes in deep-sea bamboo corals

JESSE R. FARMER^{1*}, BÄRBEL HÖNISCH¹, LAURA ROBINSON², TESSA HILL³ AND MICHÉLE LAVIGNE³

¹Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY, USA, jfarmer@ldeo.columbia.edu (* presenting author)

²Woods Hole Oceanographic Institution, Woods Hole, MA, USA lrobinson@whoi.edu

³Bodega Marine Laboratory, University of California-Davis, Bodega Bay, CA, USA, mglavigne@ucdavis.edu

Background

Deep-sea corals represent an intriguing archive for application of the boron isotope-pH proxy because of their potential for subdecadal-scale reconstructions [1] during present and past carbon system perturbations [2]. However, previous studies of boron isotopes in aragonitic deep-sea scleractinian corals showed evidence for systematic skeletal variations in $\delta^{11}\text{B}$ that could not be attributed to environmental factors [3]. In contrast to scleractinians, deep-sea gorgonian bamboo corals secrete high-magnesium calcite and may not be expected to exhibit similar $\delta^{11}\text{B}$ heterogeneity, but the boron isotopic composition of bamboo corals has not been investigated in detail. Here we present an evaluation of $\delta^{11}\text{B}$ variability from the genus *Keratoisis*, a cosmopolitan deep-sea calcitic bamboo coral.

Results

Initial results from four modern *Keratoisis* specimens collected between 500 and 2500m depth in the North Atlantic and North Pacific Oceans show that coral surface $\delta^{11}\text{B}$ positively correlates with ambient seawater pH and is consistent with borate incorporation from seawater. Samples taken at 1mm spacing across the width of individual corals shows that intra-sample $\delta^{11}\text{B}$ does not exceed 2-3 per mil. An increase in $\delta^{11}\text{B}$ toward the central growth axis of our North Pacific *Keratoisis* specimen is associated with lighter carbon and oxygen isotopes [4]. Two North Atlantic corals show increased $\delta^{11}\text{B}$ toward the surface of the outer growth surface, a result that is in contrast to the expected increased contribution of anthropogenic carbon in the deep sea. We seek to constrain the observed boron isotopic variability and coral growth rates using trace metal (B/Ca, U/Ca, Sr/Ca, Mg/Ca), stable isotope ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$), and radiocarbon analyses within our *Keratoisis* corals.

[1] Roark et al. (2005) *Geophys. Res. Lett.* **32**, L04606. [2] Robinson et al. (2005) *Science* **310**, 1469-1473. [3] Blamart et al. (2006) *Chemical Geology* **225**, 61-76. [4] Hill et al. (2011) *Geochem. Geophys. Geosys.* **12**, Q04008.