Estuarine salinity variations from bivalve shell B/Ca ratios measured *in situ* by ion microprobe (SHRIMP RG)

RENEE K. TAKESUE[1], CHARLES R. BACON[1], AND
CYNTHIA L. BROWN[2]

[1]USGS MS 910, Menlo Park, California, USA
rtakesue@usgs.gov
[2]USGS MS 465, Menlo Park, California, USA

Climate-related changes in freshwater delivery to estuaries and coastal regions may play a significant role in ecosystem function and structure. Understanding the natural (pre-anthropogenic) response of estuaries to climate variability would be valuable for restoration efforts, as well as for resource use and policy decisions. Information preserved in estuarine or nearshore sediments may enable the study of past environments. Bivalve shells appear to be promising archives of such records, because they form by accretion and because their chemical composition may reflect ambient temperature, salinity, and/or water chemistry. Boron has been investigated as an indicator of estuarine salinity, as boron concentrations in waters are proportional to total salt concentrations.

Aragonitic shells of a subtidal euryhaline bivalve, *Potamocorbula amurensis*, were collected in February 1994 (Shell 1) and April 1996 (Shell 2) near the confluence of the Sacramento and San Joaquin Rivers (San Francisco Bay, California), where salinity ranges between 0-12. Elemental boron to calcium ratios (B/Ca) were analyzed in transects along cross-sections of *P. amurensis* shells at 3-10 day sampling resolution (50 µm spot size) over fourteen months of growth using the Stanford-USGS Sensitive High-Resolution Ion MicroProbe with Reverse Geometry (SHRIMP RG). *P. amurensis* shell B/Ca ratios were quantified relative to a coral with known boron concentration. Shell B/Ca ratios followed seasonal salinity patterns and were positively correlated with bottom water salinity during periods when salinity was >~1 (r=0.74 and r=0.96). B/Ca ratios in Shell 1 varied over a 2.75-fold range, while B/Ca ratios in Shell 2, which grew during an unusually wet year, varied over a 7.25-fold range. During periods when salinity was <<1, shell B/Ca ratios varied with freshwater inflow. Inferred B/Ca values for freshwater end members were three times higher in Shell 1 than in Shell 2. These results suggest that the B/Ca ratio of the freshwater end member may vary both intra-seasonally and from year to year. Bivalve metabolic processes may also influence shell B/Ca ratios during periods when salinity <<1.

Our results suggest that elemental B/Ca ratios in aragonitic bivalve shells may be a valuable tool for reconstructing event-scale, seasonal, and interannual salinity patterns in environments such as estuaries and coastal wetlands where freshwater inflows are high. B/Ca-salinity relations will also be explored in *P. amurensis* shells growing at a site where salinity reached 28.

Methane seeps, chemosynthetic communities, and carbonate rocks on the Kuroshima Knoll, off Ryukyu islands

RIKA TAKEUCHI[1], RYO MATSUMOTO[2] AND
HIDEAKI MACHIYAMA[3]

[1] Department of Earth & Planetary Science, The University of Tokyo, Tokyo, Japan (lika@gbs.eps.s.u-tokyo.ac.jp)
[2] Department of Earth & Planetary Science, The University of Tokyo, Tokyo, Japan (ryo@eps.s.u-tokyo.ac.jp)
[3] Deep Sea Research Department, Japan Marine Science and Technology Center, Yokosuka, Japan
(bucci@jamstec.go.jp)

A series of ocean floor surveys by JAMSTEC-Deeptow camera system, ROV “Dolphin-3K”, and manned submersible “Shinkai 2000” has discovered a number of methane-seep sites, large chemosynthetic colonies and carbonate rocks atop the Kuroshima Knoll at the depth of water of 650-800 meters. The methane seeps seem to be concentrated in ~20 meters wide faulted and fractured zones in the eastern part of the Knoll. Kuroshima Knoll is flat-topped, but valley-like eroded depressions with a few to 10 meters deep were common in the eastern part, where massive, irreguraly shaped carbonate rocks (called carbonate ‘towers’) characterize the micro-morphology. Occurrence and composition of ‘towers’ suggest that they were originally formed within shallow subsurface of sulfate reduction zone, then excavated by strong bottom current.

Carbonates of the Kuroshima Knoll have various shapes and macroscopic textures. They are classified into five types; pavement, shell crust, tower, chimney, and nodule. It is clear that shell crust type is composed either of aragonite, calcite, and/or dolomite, while tower type is composed mainly of aragonite and calcite, Nodular type is composed of various mixture of calcite and dolomite. The chimney and shell crust type is composed exclusively of fine crystalline dolomite.

d^{13}C of carbonates shows light value (-48 to -8 ‰ PDB), implying a close relation to methane seeps. Light-carbon methane was oxidized by sulfate to increase [HCO_3^-] and alkalinity within shallow sulfate reduction zone, causing precipitation of carbonates. d^{18}O ranges from +2 to +8 ‰ PDB. Assuming that the carbnates were precipitated at temperatures similar to the present bottom water temperatures, the carbonate-precipitating waters are estimated to be a maximum of +1.8 in ‰ heavier than the present bottom waters. Heavy oxygen waters were presumably derived from dissociation of subsurface gas hydrates. Pressure (=depth of water) and temperature of the shallow sediments of the Kuroshima Knoll are very close to the phase boundary for the system of methane + water + gas hydrates. Even slight changes in bottom water temperatures or relative water depth may have caused dissociation of subsurface gas hydrates and increased methane flux and ventings on the seafloor.