

High resolution minor and trace element study on mussel shells from coastal region of Tatoosh Island, Washington, USA

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The successively deposited calcium carbonate layers and annual growth bands in mollusk shells could offer high resolution archives of the environmental conditions the mollusk has experienced during its life. Previous studies have shown that the elemental composition of mollusk shells is related to environmental parameters [1, 2, 3].

Here, we present high resolution data of a suite of minor/trace element/Ca ratios collected from shells of mussel species, *Mytilus californianus*, using laser ablation sector field inductively coupled plasma mass spectrometry (LA-ICP-MS) as well as an ICP-MS solution based method. The mussel shells were ~10 years of age and were collected live in 2009 and 2010 from Tatoosh Island, Washington, USA, where instrumental data of various environmental parameters over the last decade are available. We also analyzed several shells present in middens on Tatoosh Island. Radio-carbon dating data of these mussels show they lived ~1000 years ago; shell banding suggests individual ages of ~12 years. Age models were constructed using annual banding, a growth model and high resolution stable isotope composition ($\delta^{18}\text{O}$) of the shell.

Our preliminary results show that several of a suite of trace elements exhibit promising correlation with nutrient concentration and oxygen level in the sea water, and could serve as proxies for coastal geochemical cycling and a means to probe rapid changes documented in seawater chemistry at this site [4]. Data for a suite of element/Ca ratios from different transects on the same shell generally show good reproducibility. Element/Ca data from midden shells and modern shells show different ranges of variation suggesting that there have been significant differences in geochemical cycling in this coastal environment over the last 1000 years.

[1] Dodd (1965) *GCA*, **29**, 385-398. [2] Klein *et al.* (1996) *Geology*, **24**, 415-418. [3] Putten *et al.* (2000) *GCA*, **64**, 997-1011. [4] Wootton *et al.* (2008) *PNAS*, **105**, 18848-18853.

Carbonate rocks from fluid and gas expulsion sites of the Green Canyon, Gulf of Mexico: Analysis and interpretation

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Cold hydrocarbon seepage is a frequently observed phenomenon in marine settings worldwide. Authigenic carbonates from hydrocarbon seeps are unique archives of past seepage and associated environmental parameters. Carbonate rocks were collected from fluid and gas expulsion sites of Green Canyon lease block 140 (GC 140) at 260 m water depth on the Gulf of Mexico continental slope during Johnson-Sea-Link dive 2591 in 1989. The carbonate rocks occur as blocks, crusts, and nodular masses incorporated in carbonate breccias. Most carbonates are composed of aragonite and high-Mg calcite as determined from X-ray diffraction. However, one sample was found to have composition of nearly 100% dolomite. Petrographically, high Mg-calcite peloidal matrix and acicular to botryoidal aragonitic void-filling cements are the most frequent associations. The carbon isotopic compositions of the carbonates ($\delta^{13}\text{C}_{\text{car}}$) range from -36.5‰ to $+4.9\text{‰}$ V-PDB, indicating complex carbon sources that include ^{13}C -depleted methane, seawater CO_2 , and ^{13}C -enriched residual CO_2 from methanogenesis. A similarly large variability in $\delta^{18}\text{O}_{\text{car}}$ values ($+1.6\text{‰}$ to $+5.5\text{‰}$ V-PDB) demonstrates the geochemical complexity of the studied area. The considerable range of mineralogical and isotopic variations of the studied cold seep carbonate suggests that local controls on the fluid and gas flux, types of the local hydrocarbon reservoir may play an important role in determining carbonate mineralogy and isotope geochemistry. In addition, the ^{14}C ages of bivalve shells incorporated in the carbonate matrix will be used to determine the timing and duration of fluid seepage in order to provide preliminary insight into probable factors governing seepage processes at the studied site.

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