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Barium/calcium profiles of calcite and aragonite marine bivalve shells as an environmental proxy

D.P. Gillikin (1), A. Lorrain (2), Y.-M. Paulet (3), L. André (4) and F. Dehairs (5)

(1) Dept. of Earth Science and Geography, Vassar College, Poughkeepsie, NY, USA,

(2) IRD, US CHRONOS, LASAA, Centre IRD de Brest, Plouzané, France, (3) LEMAR, UMR CNRS/ Plouzané, France, (4) Section of Mineralogy and Petrography, Royal Museum for Central Africa, Tervuren, Belgium, (5) Department of Analytical and Environmental Chemistry, Vrije Universiteit Brussel, Brussels, Belgium, (dagillikin@vassar.edu / Fax: (845) 437-7577 / Phone: (845) 437-7138)

Barium/Calcium profiles of bivalve shells are characterized by flat background signals periodically interrupted with sharp peaks. Both field and laboratory data show that the flat background Ba/Ca signals in the calcitic shells of the blue mussel, *Mytilus edulis*, are correlated with Ba/Ca of the water in which they grew. The peaks however are more difficult to understand. To test if the peaks are an environmental signal related to productivity, we analyzed high resolution Ba/Ca profiles in bivalve shells that grew adjacent to one another. Two aragonitic *Saxidomus giganteus* show remarkable similarity over a decade of growth, clearly indicating an environmental forcing, but the peaks sometimes precede chlorophyll$a$ peaks suggesting no causal relationship with phytoplankton blooms. Four calcitic *Pecten maximus* shells also record synchronous Ba/Ca peaks, again indicating an exogenous control. The Ba/Ca peaks, however, start $\sim$40 days after the crash of the bloom, while sedimentation takes place immediately following the bloom. Barite formation in settling phytoplankton flocs, as has been previously proposed, is clearly not the cause of these peaks. We suggest that Ba/Ca peaks in bivalve shells are caused by an as of yet undetermined environmental forcing independent of shell mineralogy and that background Ba/Ca signals are a good indicator of environmental Ba/Ca values.