Developing Rare Earth Elements as a Paleoceanographic Proxy: Separating Primary and Diagenetic Influences

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Due to ionic radii contraction and redox effects, the Rare Earth Elements (REEs) are of interest to paleoceanographers as potential tracers of seawater oxygen content and for water mass identification. Although the use of foraminiferal calcite as a carrier for REEs has been limited because of contamination issues (Palmer, 1985), the primary REE patterns preserved in planktonic, epifaunal and infaunal foraminifera shells should provide unique information about changes in chemistry, productivity and bottom water oxygen over time. As such, the ability to measure REEs in foraminiferal calcite would be of great value in paleoceanographic and paleoclimatic studies.

Unfortunately, ~90% of the REE content measured in forams is believed to be in oxide "coatings" (Palmer, 1885). This is potentially problematic as traditional "batch" leaching procedures may not work for REEs, since they appear to undergo re-adsorption during these procedures (Sholkovitz, 1989). We have overcome these problems with a "flow-through" leaching procedure in which REEs from Mn and Fe coatings are flushed from the system (and trapped down-stream) as the cleaning proceeds. Our approach is to use an ion chromatograph and oven system to control the chemical conditions (reagent proportions and concentrations) and physical conditions (timing, pressure, temperature) of the leaching. This system also allows us to monitor eluent from any stage of the leaching process as phase indicators, in order to assess cleaning efficiency. This system will help develop and standardize cleaning techniques, with the ultimate goal to derive a leaching scheme that allows measurement of elements in the original calcite. Preliminary data from development of leaching methods will be presented. The application of these cleaning methods to paleostudies using REEs and other elements will be discussed.

Specifically, foraminiferal calcite as a paleotracer will hinge upon comparisons between REEs in the calcite versus REEs in the water in which that foraminifer lived: surface ocean, bottom water, pore water. This comparison is essential to ground-truthing foraminiferal REE patterns as a paleoproxy. The comparison of REEs in the living environment to the cleaned calcite will make interpretation of the signal possible. Additionally, comparing the calcite REE patterns to pore water REE patterns will help elucidate the affects of diagenesis on foraminiferal REEs. Such measurements have been made possible only recently with more powerful mass spectrometers and advanced ion chromatographic techniques. We will employ these techniques to determine REE signals in bottom and pore waters from sediments exhibiting a range of oxic conditions for comparison with foraminiferal REEs from the same sediments. These data will help us determine if REEs in the foraminiferal calcite undergo diagenetic alteration and the relation between oxide coatings and pore water REEs. These pore water data will also be important in constraining the geochemistry of REEs in the oceans.

Palmer MR, *Earth and Planetary Science Letters*, **73**, 285-298, (1985).

Sholkovitz ER, *Chemical Geology*, **77**, 47-51, (1989).