High-Precision Low-Blank Lithium Isotope Ratios in Forams

Sambuddha Misra (NHMFL & Oceanography Department, FSU) and P. N. Froelich (NHMFL & Oceanography Department, FSU)

Introduction

The lithium isotope ratio of seawater (\(^7\text{Li}/^6\text{Li}\)) is preserved in the calcite shells of marine planktonic foraminifera, providing a potential recorder of changes in this ratio in seawater through geologic time. We theorize that this isotope ratio should not be constant with time but rather display variations linked to changes in processes that control the major cation and anion composition of the ocean – chemical weathering of the continents (erosion and river fluxes), hydrothermal weathering of seafloor basalts (hot spring fluxes) and reverse weathering of seafloor sediments and basalts (diagenetic fluxes). Each of these silicate sources and sinks to/from the sea carry unique \(^7\text{Li}/^6\text{Li}\) signatures and very large fractionation factors, providing a unique time tracer of changes in the global silica cycle that may be diagnostic of long-term variations in seawater chemistry. A long (Cenozoic = 65 million years) \(^7\text{Li}/^6\text{Li}\) record of seawater would complement existing records of seawater chemistry change such as strontium, osmium and sulfur isotopes.

Experimental

This work established a new Quad ICP-MS method to measure \(^7\text{Li}/^6\text{Li}\) at low Li concentrations in forams (1-2 ppm) on less than 0.5 ng-Li (several dozen individual shells) and yielding isotope ratio precisions of better than one per mil (2-sigma) and blanks of less than 0.5 pg/mL. These analytical figures of merit are several orders of magnitude better than other methods using TIMS and MC-ICP-MS. The primary advantage of Quad ICP-MS method is the capability to realize and control very low blanks during column separations to remove other cations (alkalis and alkaline earths interfere in the mass spectrometry) and demonstrate 100% yields to eliminate fractionation on and off the column. Matrix effects of Na and Ca and of column chromatography on Li isotope ratios were investigated using artificial Li (LSVEC) solutions representative of foram compositions (matrix matching). A single step chromatographic method to quantitatively separate Li from matrix elements uses small volume resin (3.4 meq/2mL AG50W-X8) and acid (6mL 0.5N HCl). \(^7\text{Li}/^6\text{Li}\) ratios in the eluents are then measured with an Agilent 7500cs in cold plasma (600 W – eliminates plasma and doubly charged \(^{14}\text{N}\) and \(^{12}\text{C}\) interferences while fully ionizing Li due to its low ionization potential). Column yields are shown to be better than 99.99%.

Results and Discussion

Analyses of core top (recent) foram shells by species and by size class are in progress at this writing. Two ocean drilling sites have been selected to generate the first \(^7\text{Li}/^6\text{Li}\) records. Samples have been obtained from the 0-14 million year interval of ODP (Ocean Drilling Project) Site 926 from the Ceara Rise (Equatorial Atlantic) and from the 0–3 million year interval of DSDP (Deep-Sea Drilling Project) Site 758 atop the Ninetyeast Ridge in the northern Indian Ridge.

Conclusions

New Quad ICP-MS and column chromatography methods were developed to measure \(^7\text{Li}/^6\text{Li}\) ratios in marine foraminifera shells and is being applied to two ocean drill site cores to generate the first Cenozoic record of lithium isotopes in seawater.

Acknowledgements

This work was funded over the years by the National Science Foundation (Marine Geology and Geophysics), The American Chemical Society (Petroleum Research Fund) and the FSU Research Foundation (Eppes Society).

References