# Lithium Isotope Ratios in Marine Forams – A Proxy for the Geologic Evolution of Seawater Chemistry through the Cenozoic

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## Introduction

The lithium isotope ratio of seawater ($^{7}Li/^{6}Li$) is preserved in the calcite shells of marine planktonic foraminifera, providing a recorder of changes in this ratio in seawater through geologic time. This isotope ratio displays secular variations linked to changes in processes that control the major cation and anion composition of the ocean – chemical weathering of the silicate continents (erosion and river fluxes), hydrothermal weathering of seafloor silicate basalts (hot spring fluxes) and reverse weathering in seafloor sediments and basalts (diagenetic fluxes precipitating authigenic silicates). Each of these silicate sources and sinks to/from the sea carry unique $^{7}Li/^{6}Li$ signatures with very large fractionation factors, providing a unique time tracer of changes in the global silica cycle that is diagnostic of long-term variations in seawater chemistry. We report here the first long (25 Ma) Late Cenozoic $^{7}Li/^{6}Li$ record of seawater verified by exhaustive foram chemical cleaning to remove contaminant phases and recrystallization artifacts, extensive multiple individual species analyses to test species offsets, and complementary "bulk" foram analyses to verify the observed long-term $^{7}Li/^{6}Li$ change. Our new record complements existing records of seawater chemistry change such as strontium, calcium, osmium and sulfur isotopes.

## Experimental

We created a new Quadrupole ICP-MS method for low Li concentrations (forams ~1-2 ppm) with <0.3 ng-Li (several dozen shells or 10 µL seawater), isotope ratio precisions <0.9 per mil (2-sigma) and blanks less than 0.5 pg/mL, several orders of magnitude better than methods using TIMS and MC-ICP-MS. Our single-step microcolumn separation method removes other cations (alkalis and alkaline earths interfere in the mass spectrometry). Elutions demonstrate >99.99% yields that eliminate $^{7}Li/^{6}Li$ fractionation on and off the column, a major problem with previous lithium isotope work. Our chromatographic method uses small volume resin (3.4 meq/2mL AG50W-X8) and acid (6mL 0.5N HCl). $^{7}Li/^{6}Li$ ratios in the eluents are measured with an Agilent 7500cs in cold plasma (600W eliminates plasma and doubly charged $^{14}N$ and $^{12}C$ interferences).

## Results and Discussion

See Figure: Coretop forams carry today's seawater $^{7}Li/^{6}Li$ ~31‰. Down core forams record an upshift in the seawater ratio of about 4‰ between 14 & 7 Ma from a previous low stand of ~27‰ (25-14 Ma) to a new high stand of ~31‰ 7-0 Ma). This change in seawater $^{7}Li/^{6}Li$ requires enormous increases in either silicate weathering fluxes and weathering intensity, or dramatic changes in the lithium sink (silicate reverse weathering), or both, suggesting an increase in $[Li]_{ocean}$ during this period of Mid-Late Miocene climate deterioration signaled by parallel changes in seawater $^{40/44}Ca$, $^{87/86}Sr$, $^{18}O$ and $^{13}C$.

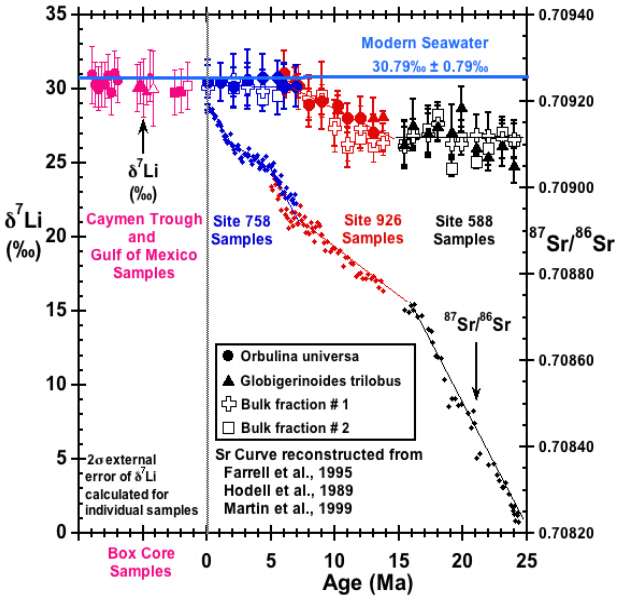


Figure. $^{7}Li/^{6}Li$ and $^{87}Sr/^{86}Sr$ record of seawater

## Conclusions

Seawater $^{7}Li/^{6}Li$ increased dramatically between 14-7 Ma ago.

## Acknowledgements

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## References

[1] Misra, S. & P. N. Froelich, EOS Trans. AGU **89**(53) Fall Meet. Suppl., Abstract v43C-1270 (2008).