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Li Isotopic Composition of Foraminiferal Tests: A Possible Proxy for Li Isotopic Composition of the Sea Water

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Isotopic composition of lithium is potentially a powerful tracer of geochemical processes such as high-temperature magmatic differentiation, alteration of oceanic crust or fluid-rock interactions. Lack of analytical techniques capable of high-sensitivity, precise, and accurate measurements in the past has precluded detailed study of Li isotopic composition in geological materials and its fluxes between different reservoirs. As a result, the global lithium mass balance is only poorly understood: the two major sources of oceanic lithium (expressed as δ^6Li values calculated relative to ^{6}Li/^{7}Li$_{\text{L-SVEC}}$ = 0.0832) are river input from the continents (-6 to -32.2‰) and high-temperature alteration of oceanic basalts (-9‰). Given the average sea water Li isotopic composition of -32‰, additional inputs or sinks that fractionate Li isotopes are required to maintain a steady state of Li isotopes in the oceans. If a proxy for the Li isotopic composition of past oceans could be developed, it would provide us with invaluable information about the variation in rates of continental weathering and/or sea floor spreading.

Inductively coupled plasma mass spectrometry (ICPMS) is a technique that can provide routine, precise and accurate (and relatively inexpensive) measurements of Li isotopic composition in geological materials that need to be studied to constrain the inputs and sinks to the Li geochemical cycle. Using a VG PQ3 quadrupole ICPMS with a cool plasma, isotopic composition of lithium can be measured with a within-run precision of 0.05‰ (standard error of the mean), and a long term reproducibility of standards better that 2‰ (2 σ). Similar to other techniques that are currently in use to analyse Li isotopic composition, quantitative chemical separation of Li prior to the measurement on ICPMS is necessary to avoid the matrix-induced isotopic fractionation and the results have to be externally corrected for mass bias and instrumental fractionation. On the other hand, the low-blank chemistry (total blank of ca 120 pg Li) and high Li ionisation efficiency allow precise measurements of isotopic ratios from concentrations as low as 5 ppb Li. Using a low sample uptake, samples containing 5 - 10 ng Li can be analysed without compromising the sensitivity and time of the measurement.

We have successfully analysed 5 - 10 mg samples of planktonic foraminiferal tests (*Pulleniatina obliquiloculata*, *Globorotalia tumida* and *Orbulina universa*) from top 2 cm of cores collected from the Ontong-Java Plateau (western Pacific) and Ceara Rise (western equatorial Atlantic). The samples were crushed to break open the chambers and ultrasonically and chemically cleaned prior to dissolution to avoid contamination by Li from surface coatings or host sediment. The studied tests contain 0.7 - 1 ppm Li and their Li isotopic composition varies from -27.1 to -57.9‰. Our limited data show a variable Li isotopic composition for *Globorotalia tumida* and *Orbulina universa*. Isotopic composition of Li in *Pulleniatina obliquiloculata* is similar to that of the present day sea water and it is independent of the size of the tests. This suggests that its composition is not affected by growth history or isotopic exchange with the sediment. Hence, this species may be used as a proxy for Li isotopic composition of the sea water. The variation in the Li isotopic composition among the three species and within the first two species indicates that fractionation of Li isotopes occurs during the precipitation of foraminiferal calcite. It is as yet unclear what thermodynamic or biological processes control the fractionation. Nevertheless the differences among the species indicate that this process must be accounted for to develop a robust and reliable proxy of past variation in Li isotopic composition of the ocean water.