



In situ measurements of Li isotopes in foraminifera

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It has been estimated that the main sources of dissolved lithium to the oceans ($\tau=1.5\text{Ma}$) are the continental flux (8.10^9 mol/yr) and the hydrothermal flux (14.10^9 mol/yr). As a consequence, Li/Ca and $\delta^7\text{Li}$ measured in foraminifera for the past 75Ma should give essential information about variations of seawater composition, the continental flux, and potentially silicate weathering rates. It is also possible that Li/Ca content and $\delta^7\text{Li}$ measured in marine carbonates are controlled by environmental conditions (water temperature, growth rates). Until now, there is no consensus about $\delta^7\text{Li}$ measurements of past foraminifera. In more detail, Hall (2002) measured a constant $\delta^7\text{Li}$ for *Orbulina universa* for the past 40ka. In contrast, *Euvigerina*, *P. obliquiloculata* and *G. tumida* display significant variations through time (You and Chan (1996); Hoefs and Sywall, (1997); Kosler et al. (2001)), with sometimes contradictory results. Similarly, it seems difficult to explain Li/Ca range and variations measured within and between foraminifera species (Hall et Chan, 2004; Marriott et al., 2004).

Published $\delta^7\text{Li}$ data for foraminifera have been measured by MC-ICP-MS, ICP-MS or by TIMS from batches of 20-50mg of foraminifera. These techniques all need a specific and delicate cleaning procedure before Li elution and isotopic analyses, in order to remove contaminating non-carbonate components.

We have developed *in situ* measurements of Li isotopic ratios in foraminifera using a Cameca ims 1270 ion microprobe (CRPG, Nancy). The main advantages of *in situ* measurements are first the possibility of checking isotopic homogeneity of single foraminifera, and then to avoid visible potential contamination coming from pores and from the coating. The procedure used for Li isotopic measurements in calcite is very similar to that used by Chaussidon et al. (1997) on the ims 3f. Isotopic analyses were performed using a 20-30 μm 60nA $^{16}\text{O}^-$ primary beam.

We first analysed Li isotopic ratios in a few foraminifera from the West-Pacific (22°S, 161E, *Orbulina universa*). Results show an internal error of less than 1 per mil after a 20 min run. External error is 1.2 per mil at 2σ level, showing a good isotopic homogeneity within and between foraminifera. Results obtained for *Truncorotalia tosaensis* (1.1Ma), *Globorotalia inflata* (2Ma) and *Globiigerina* (2Ma) from ODP Leg 198 (Shatski Rise) display much less reproducible results (with internal errors up to 6 per mil, although the mean (uncorrected) value is only 2 per mil lower than *Orbulina*). The large uncertainties for these samples are systematically associated with large increases of lithium concentrations.

Ion imaging was performed by SEM and ion microprobe (Aleo et al., 2001) in order to localise and characterize Li-rich phases in the Shatsky Rise foraminifera. Ion imaging of Mg, Al, Si, Ca and Li highlights the presence of isolated but numerous 1-3 μ m alumino-silicate grains, apparently embedded within the chamber-wall calcite. Li image treatments (associated with Al and Si) allow us to estimate variable and high Li contents in these micrometric grains, at up to 100 times the Li contents measured in the surrounding calcite. The same polishing and sample pre-treatment for ion probe analysis has been used for measuring Li isotopes and contents in scallop shells and CARB calcite standard. No significant increase in Li intensity was observed for about 30 analyses. The assimilation of small Al-Si grains by foraminifera during their calcification process is considered.