

## In situ measurements of Li isotopes in foraminifera

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[1] In situ measurement of Li isotope ratios in foraminifera has been developed using a Cameca ims 1270 ion microprobe. In situ  $\delta^7\text{Li}$  analyses have been performed in biogenic calcite of planktonic foraminifera from various locations. Results show that for west Pacific mixed *Globigerinoides* and *Globorotalia* ( $22^\circ\text{S}161^\circ\text{E}$ ), the isotopic variability between tests and within a single test, respectively, is not significantly greater than estimated analytical uncertainty ( $\sim 1.5\text{‰}$ ). Mean  $\delta^7\text{Li}$  for several planktonic foraminifera tests corresponds to the seawater value, strongly suggesting negligible Li isotope fractionation relative to seawater, as previously inferred by Hall et al. (2005) using thermo-ionization mass spectrometer and multicollector-inductively coupled plasma-mass spectrometry techniques. Combined with scanning electron microscopy and ion microprobe imaging, micron-sized grains, enriched in lithium, silica and aluminum have been found in the foraminifera calcite matrix. A simple mixing model shows that 0.3–2 wt % of marine clays incorporated within the analyzed calcite would lower the foraminifera  $\delta^7\text{Li}$  value, by 3‰ to 10‰ relative to the isotopic composition of the pure calcite. By comparison, no such grains have been detected in corals. The presence of micron-sized silicate grains embedded within the foraminifera calcite is consistent with the Erez (2003) biomineralization model, involving calcite precipitation from seawater vacuoles. By contrast, coral calcium carbonate is instead precipitated from ions, which have been pumped or diffused through several membranes, impermeable to micrometric grains. Ion microprobe in situ  $\delta^7\text{Li}$  measurements in biogenic calcite present new methods for investigating both biomineralization processes and the past record of the ocean composition by exploring geochemical variations at a scale that is smaller in space and in time.

## 1. Introduction

[2] Lithium is a powerful tracer of water-rock interactions, because of its great potential to be mobilized by water. The two main sources of dissolved lithium in the oceans are considered to be (1) the continental flux ( $8 \times 10^9$  mol Li/yr,  $\delta^7\text{Li} = 23\%$ , with  $\delta^7\text{Li} = 1000((^7\text{Li}/^6\text{Li}) - (^7\text{Li}/^6\text{Li})_{\text{LSVEC}}) / (^7\text{Li}/^6\text{Li})_{\text{LSVEC}}$  [Huh *et al.*, 1998]) and (2) the hydrothermal flux ( $3\text{--}8 \times 10^9$  mol Li/yr,  $\delta^7\text{Li} = 9\%$  [e.g., Chan *et al.*, 2002]). Li/Ca and  $\delta^7\text{Li}$  oceanic paleovariations are therefore expected to place important constraints on past silicate weathering rates [Hathorne and James, 2006]. Another possibility is that Li/Ca ratio and  $\delta^7\text{Li}$  measured in marine carbonates are controlled by environmental conditions at the time of precipitation, in particular water temperature and growth kinetics. The ocean residence time of lithium has been estimated to be about 1.5 Ma [Huh *et al.*, 1998], implying that Li isotopes measured in marine sediments can hardly display ocean source paleovariations with a frequency lower than 1 Myr.

[3] The  $\delta^7\text{Li}$  value for the ocean is  $31.2\% \pm 0.5\%$  [e.g., Millot *et al.*, 2004; Carignan *et al.*, 2004] and quantification of the isotopic fractionation during foraminifera growth is still debated. Experimental growth studies demonstrate that  $\delta^7\text{Li}$  for inorganic calcite is 2‰ and 9‰ lower than the solution composition (seawater and pure Li solution, respectively). The  $\delta^7\text{Li}$  values for the benthic species *Uvigerina* of the Arabian Sea are 5‰ lower than the seawater value [Marriott *et al.*, 2004b]. Hall *et al.* [2005] measure no isotopic fractionation relative to seawater for the planktonic species *Orbulina universa*, *Globigerinoides sacculifer*, *Globorotalia menardii* and *Truncorotalia truncatulinoides*. By contrast, Hathorne and James [2006] highlight significant isotope fractionation for some foraminifera species (e.g., *T. truncatulinoides*, *Nq. dutertrei*, *Gr. tumida*) and negligible fractionation for others (e.g., *O. universa*). Finally, a study of Kössler *et al.* [2001] shows a wide range of  $\delta^7\text{Li}$  (29–48‰) for core top *Globorotalia tumida* sampled in various locations.

[4] There is also significant discrepancy in  $\delta^7\text{Li}$  and Li/Ca data for past foraminifera. According to You and Chan [1996], *Uvigerina* and *Pulleniatina obliquiloculata* display significant  $\delta^7\text{Li}$  paleovariations (e.g., from 19‰ to 40‰ for the 400–800 ka period). Measurements of mixed foraminifera also yield a wide range of  $\delta^7\text{Li}$  from 10‰ to 40‰ since the beginning of the Eocene period [Hoefs and

Sywall, 1997]. More recently, Hathorne and James [2006] found much smaller  $\delta^7\text{Li}$  oceanic variation ( $\delta^7\text{Li}$  range is 26–31‰ for the 0–18 Ma period), and Hall *et al.* [2005] showed no change in seawater  $\delta^7\text{Li}$  during the last glacial-interglacial transition. This is more in agreement with experiments since it has been shown that the calcite Li isotope composition does not vary significantly (<2‰) in case of great temperature or salinity change (5–30°C and 10–50 psu, respectively [Marriott *et al.*, 2004a, 2004b]).

[5] Li/Ca ratios measured in foraminifera are also difficult to interpretate. The role of temperature remains unclear since Li/Ca display constant, positive or negative trends as a function of temperature, sometimes even for the same species, depending on the location [Hall and Chan, 2004]. Experimental inorganic calcite precipitation shows that Li/Ca ratios decrease significantly with increasing temperature (a factor  $\sim 3$  over 25°C). A controlling role of the growth rate has been inferred [Marriott *et al.*, 2004a]. Hathorne and James [2006] found a negative correlation between  $\delta^7\text{Li}$  and Li/Ca for recent foraminifera, attributed to a species and a biomineralization effect. The interpretation of  $\delta^7\text{Li}$  paleovariations depends on whether or not this effect is taken into account.

[6] Overall, published studies clearly highlight unexplained and sometimes contradictory ranges of  $\delta^7\text{Li}$  and Li/Ca measured in foraminifera. These data could partly reflect significant variability within a species or within a single test, as has been shown for strontium in *Ammonia batavus* [Allison and Austin, 2003]. These intratest variabilities for lithium are not detectable with existing techniques. Indeed, Li isotope measurements in foraminifera are limited by the low level of lithium in calcite (ppm level). About 20–50 mg of foraminifera are needed for a reliable isotopic analysis using multi-collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS). Hence batches of several foraminifera ( $\sim 10\text{--}50$ ) are required for measurement. Another complication relies on the potentially significant contamination by noncalcitic material accumulated in the external coating, inside chamber cavities and pores, which is thought to be acquired after the test deposition on the seafloor. Prior to analyses, foraminifera batches need to be carefully precleaned and crushed in order to eliminate all this contaminant lithium [Marriott *et al.*, 2004b].

[7] Intratest measurements of trace elements in foraminifera are still scarce and, although electron

microprobe is suitable for measuring Mg and Sr contents [e.g., *Brown and Elderfield*, 1996], this technique is not applicable for light elements like lithium. Laser ablation (LA)-ICP-MS measurements of Li/Ca in precleaned foraminifera were performed by *Hathorne et al.* [2003], and highlight, for *Globorotalia tumida*, significant intratest variability. The use of the ion microprobe to study the variability of trace element in foraminifera has recently been developed by *Allison and Austin* [2003]. There are several potential advantages in the use of the ion microprobe. First, the microprobe can be focused on area free from any detrital material, without test precleaning. Then, based on intact tests, it is possible to study the internal variability of lithium and its isotopes by measuring several spots in the same test. Finally, it is also possible to individually measure several foraminifera of the same age and species. Whole tests of nonprecleaned foraminifera have been used for in situ Sr and Mg analyses [*Allison and Austin*, 2003]. Mg contents were strongly affected by contaminant silicate grains and data filtering was done based on Li, Si, and Al contents measured in the same spots.

[8] Here we describe for the first time a technique for determining Li isotope composition within individual foraminifera tests by ion microprobe. We present some preliminary results that demonstrate the validity of the technique. However, combined with imaging using 1270 ion microprobe and scanning electron microscopy (SEM), we also highlight limitations in determining Li isotope composition in foraminifera due to the presence of Li-rich aluminosilicate micron-sized grains embedded within the calcite matrix.

## 2. Methods

### 2.1. Samples and Standards

[9] All the details about samples and standards used in this study are described in the auxiliary material<sup>1</sup>.

### 2.2. Element Cartography With SEM

[10] A 20 keV focused beam of electrons is rastered across a sample surface, the raster scan being synchronous with that of a cathode ray tube (CRT). The brightness of the CRT is modulated by the detected secondary electron current coming from

the sample, such that the CRT displays an image of the variation of secondary electron intensity. This variation is dependent on the incidence angle of the focused beam onto the sample, thus yielding a topographical image. Qualitative and semiquantitative chemical analysis information can also be obtained using an energy dispersive X-ray spectrometer associated with the SEM. In this study, we used the dispersive X-ray spectrometer of the SEM to produce elemental maps of C, O, Al, Si and Ca.

### 2.3. Ion Microprobe Measurements

[11] Analyses were performed using the Cameca ims 1270 ion probe at the CRPG, Nancy, France. Foraminifera in gold-coated ring were analyzed with a  $^{16}\text{O}^-$  primary beam, accelerated at 13 kV. We used two different settings. The first one was used for Li isotope analyses, and the second one corresponds to ion imaging acquisition (see Table S1 of auxiliary material for summary).

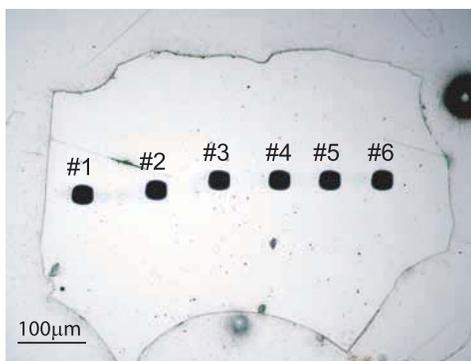
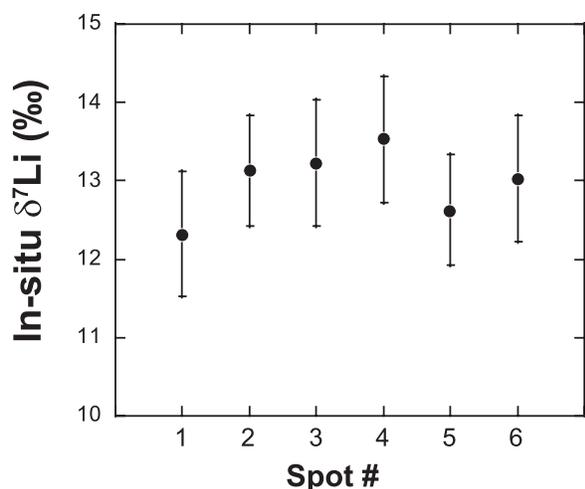
#### 2.3.1. Analytical Procedure for Li Isotope Analyses

[12] The procedure used for Li isotope measurements with the Cameca ims 1270 ion probe is adapted from that described by *Chaussidon and Robert* [1998] with the Caméca ims 3f and by *Rollion-Bard et al.* [2003] for boron isotope analyses. The lithium isotopic compositions were measured by in situ spot analysis, using a 20- to 30- $\mu\text{m}$   $^{16}\text{O}^-$  primary beam of  $\sim 60$  nA for both the foraminifera and the CAL-HTP calcite, 8 to 60 nA for Nazca glass, and 0.5 nA for GB-4. The mass resolving power (MRP) was set to  $\sim 3000$ , with the energy slit well centered and fully opened (Table S1). A single Li isotope analysis consists of peak switching on 6 and 7 masses, which are successively counted on an electron multiplier. After a 2 min presputtering, each run lasts  $\sim 6$  min for the glass standards (25 cycles of 6 s for  $^6\text{Li}^+$  and 4 s for  $^7\text{Li}^+$ ), and  $\sim 20$  min for the foraminifera and the calcite standard (40 to 60 cycles of 12 s and 10 s, respectively). Background is measured at mass 5.5.

#### 2.3.2. Correction of Instrumental Mass Fractionation

[13] The instrumental mass fractionation (IMF) of Li isotopes is defined as the bias between the true  $\delta^7\text{Li}$  value and the measured  $\delta^7\text{Li}$ . This instrumental fractionation can be dependent on the sample composition and structure [*Deloule et al.*, 1992]. In order to calculate the true  $\delta^7\text{Li}$  for the analyzed

<sup>1</sup>Auxiliary material data sets are available at <ftp://ftp.agu.org/apend/gc/2006gc001432>. Other auxiliary material files are in the HTML.



**Figure 1.** In situ  $\delta^7\text{Li}$  analyses performed in a single grain of CAL-HTP calcite standard. The corresponding spots are displayed on the picture underneath.

samples, we also measure a reference material with an identical matrix and a known isotopic composition. Nazca glass is used as a preliminary step for checking reproducibility and accuracy of the ion probe. We use GB-4 in order to estimate instrument fractionation for Nazca (section 2.1.2). For the foraminifera, the synthetic calcite standard (CAL-HTP, section 2.1.3) is analyzed in order to estimate the instrument fractionation. The IMF drift was considered as negligible for a  $\sim 20$  hour session, due to the constancy of the measured  $^7\text{Li}/^6\text{Li}$  ratios, in particular for GB-4 glass, measured at the beginning and at the end of the session.

### 2.3.3. Li-Al-Si-Ca Ion Imaging

[14] The full details of the microbeam technique are described by *Aléon et al.* [2001]. This technique uses a scanning beam mode. Before the ion imaging acquisition, 5-min presputtering with a 2nA primary beam was applied to remove the gold

coating on a  $50 \times 50 \mu\text{m}$  area. A  $3\text{-}\mu\text{m}^{16}\text{O}^-$  beam of 40 pA was then rastered over a defined area (e.g.,  $40 \times 40 \mu\text{m}$ ).  $^7\text{Li}^+$ ,  $^{27}\text{Al}^+$ ,  $^{28}\text{Si}^+$  and  $^{40}\text{Ca}^+$  secondary ions were detected on an electron multiplier (EM), and an image was computed by associating the measured intensity with each position of the oxygen primary beam. Ion measurements were made using the electron multiplier (EM) in a peak jumping mode. Ten cycles were measured, each cycle consisting of 100 s on  $^7\text{Li}^+$ , 50 s on  $^{27}\text{Al}^+$ , 50 s on  $^{28}\text{Si}^+$ , and 50 s on  $^{40}\text{Ca}^+$ .

## 3. Results

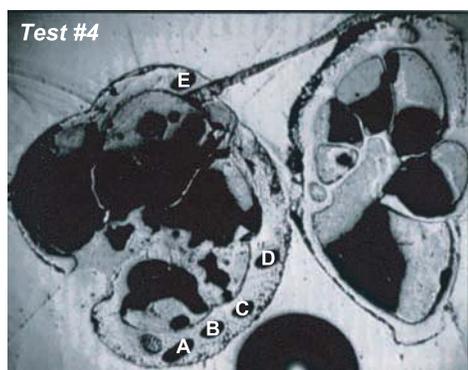
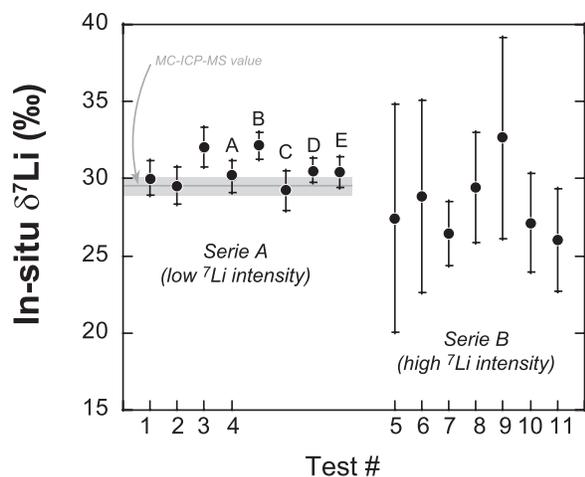
### 3.1. Reproducibility

[15] We first check the reproducibility of the in situ isotope measurements performing several analyses into silicate glass standards assumed to be isotopically homogeneous (Nazca and GB-4). The internal standard error (noted  $2\sigma_m$ ) for GB-4 estimated with the 25 cycles run is  $\sim 1\%$  (not shown here). The external reproducibility at the  $2\sigma$  level, is  $\sim 1.6\%$  and reflects the uncertainty given by several spots (3–10) measured on both silicate glasses.

[16] Because of the low Li level in carbonates, the  $^7\text{Li}^+$  intensity is divided by more than 10 when compared with silicate glass. However, this can be partly balanced by increasing the primary beam intensity. We were able to confirm that the primary ion beam intensity had a negligible effect on the instrumental mass fractionation by measuring several spots in Nazca glass, for beam intensities between 8 nA and 60 nA. The measured  $\delta^7\text{Li}$  is identical within analytical uncertainties:  $4.5\% \pm 1.4\%$  (at the  $2\sigma$  level) with the 60nA beam, and  $4.3\% \pm 3.2\%$  using the 8nA beam (see Table S2 of the auxiliary material).

[17] We checked the isotopic homogeneity of the CAL-HTP calcite standard by measuring several spots in a single  $700\text{-}\mu\text{m}$ -long grain (Figure 1). The standard deviation was  $0.4\%$ , indicating that this standard is homogeneous within analytical uncertainties. This is not surprising since this calcite was grown at high temperature ( $550^\circ\text{C}$ ) where isotopic fractionation is not expected to be significant.

[18] Measurements were performed for four different tests of west Pacific foraminifera, and showed good reproducibility at the  $2\sigma$  level ( $1.9\%$ ). Corresponding internal errors were  $\sim 1.1\%$  ( $2\sigma_m$ ). These uncertainties are similar to the uncertainties obtained with silicate glasses. Several measurements were also performed in a single foraminif-



**Figure 2.** The  $\delta^7\text{Li}$  measured in situ with the 1270 ion microprobe for various foraminiferal tests. Several spots (A–E) were also performed in a *Globorotalia inflata* single test (see picture) and show isotopic homogeneity with an external error of 2.1‰. The spots are systematically located in the internal part of the chamber walls, away from external coating and chamber cavities. Runs characterized by a significant increase of  $^7\text{Li}$  intensity during the run are labeled as Serie B foraminifera (see Table S2 and text for more details). Other runs characterized by constant (and low)  $^7\text{Li}$  intensity through time are labeled Serie A.

eral test (*Gr. inflata*, see Table S2) and yielded a  $\sim 2.1\%$  external reproducibility ( $2\sigma$ ). These results highlight isotopic homogeneity (relative to given uncertainties) within a single test and between tests for these planktonic foraminifera (Serie A foraminifera, Table S2).

### 3.2. Accuracy

[19] IMF corrected values for Nazca glass were obtained using GB-4 measurements and give a mean  $\delta^7\text{Li} = 5.0\%$  ( $\pm 0.6\%$ ,  $2\sigma_m$ ), which is in agreement with published values for Nazca and other mid-ocean ridge basalt (MORB) glasses

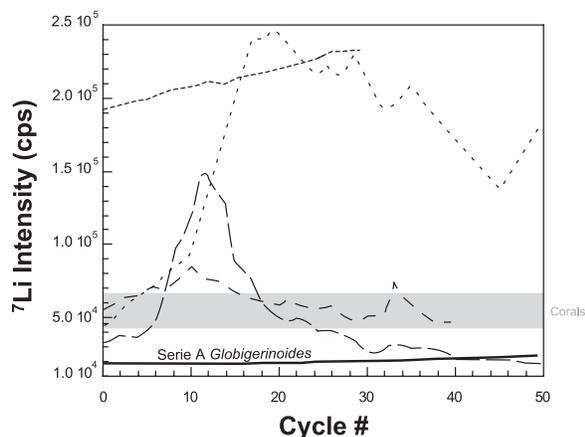
[Chan et al., 1992; Beck et al., 2006]. Both glasses are measured using two different primary beams but we consider that there is no effect of beam intensity on the IMF (Table S2, section 3.1). Typically, uncorrected  $^7\text{Li}/^6\text{Li}$  for GB-4 is  $\sim 12.41$ . The  $^7\text{Li}/^6\text{Li}$  ratio for LSVEC has recently been reestimated by Qi et al. [1997] to 12.1773, which implies a  $\sim 23\%$  IMF during in situ measurements of a silicate matrix. This is consistent with published values [e.g., Beck et al., 2006]. However, the chosen absolute value for LSVEC  $^7\text{Li}/^6\text{Li}$  ratio does not influence the corrected  $\delta^7\text{Li}$  values since the same ratio is used for both, standards and samples.

[20] For foraminifera, typical uncorrected  $^7\text{Li}/^6\text{Li}$  is  $\sim 12.39$ , which is close to the uncorrected ratios obtained for silicates, and indicates  $\sim -14\%$  IMF during in situ Li isotope analyses of carbonate matrix. The average foraminifera (Serie A)  $\delta^7\text{Li}$  value, IMF-corrected using in situ measurements performed in CAL-HTP, is  $30.5\%$  ( $\pm 2\%$  at the  $2\sigma$  level), which is equal to the seawater value ( $31.2\% \pm 0.5\%$ ), within analytical uncertainties. This is in full agreement with other studies, and in particular with thermo-ionization mass spectrometer (TIMS) and MC-ICP-MS measurements performed by Hall et al. [2005] for the same foraminifera species. The average foraminifera  $\delta^7\text{Li}$  is also equal to the MC-ICP-MS value for the same batch ( $29.5\% \pm 0.5\%$ , Figure 2 and Table S3 of auxiliary material).

[21] These results overall strongly suggest the good accuracy of the in situ Li isotope analyses performed with the 1270 ion microprobe.

### 3.3. Limitation

[22] In common with Sr and Mg ion microprobe analyses [Allison and Austin, 2003], Li analyses in foraminifera tests have encountered sample heterogeneity problems. Despite optimization of the size and location (avoiding pores and external layer) of the primary beam on the sample, Li intensity was found to increase significantly during the course of a significant number of analyses (see Figure 3). While for Nazca, CAL-HTP and some spots performed in foraminifera (Serie A foraminifera), the count rate does not vary significantly throughout the run (between 4% and 25%), the  $^7\text{Li}^+$  signal can increase by a factor of up to 50, and this in spots located far from the external coating and chamber cavities (labeled Serie B foraminifera, see Table S2 and Figure 3). Li signal rise cannot be attributed to contamination by the surrounding epoxy resin

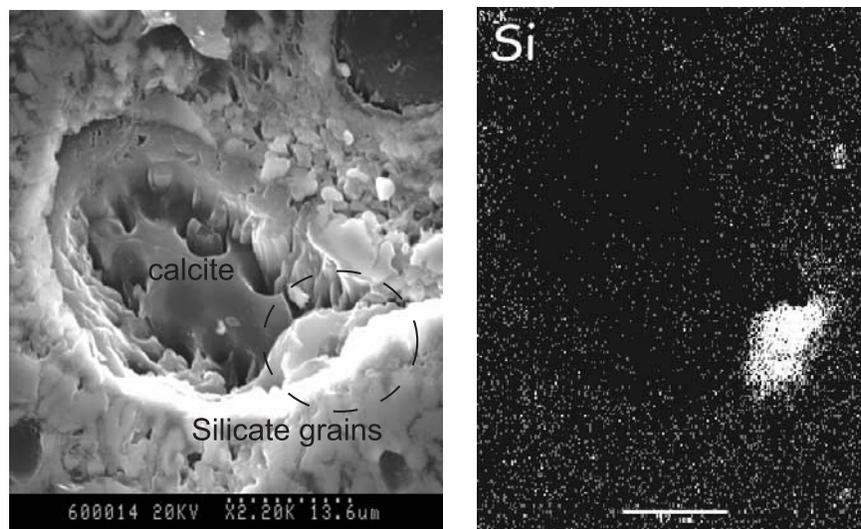


**Figure 3.** Typical variations of Li intensity during in situ isotope measurements for foraminifera. Serie A foraminifera are characterized by constant and low Li signal, whereas Serie B foraminifera are characterized by significant and unpredictable Li rise during the course of the analyses (dashed lines). We estimate that ~75% of the in situ analyses are affected by this Li rise. For comparison, the range obtained for 30 measurements of  $^7\text{Li}$  intensity in modern corals is also shown (43,800 cps to 66,600 cps with a mean value of 54,480 cps): no such effect is observed.

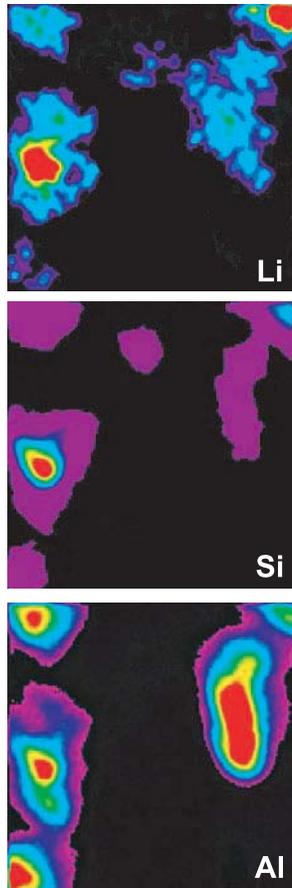
since it has been checked that the Li intensity of the resin is equal to the EM background level (~0.1 cps). Also, when compared with a “normal” run,  $^7\text{Li}/^6\text{Li}$  ratios measured during these variable

Li intensity runs display internal errors that are significantly greater (Serie B in Figure 2). However, the average uncorrected ratio is either not significantly different or lower than a normal, low Li run, suggesting the presence of silicate material with a similar uncorrected ratio, and therefore with low  $\delta^7\text{Li}$  (see section 3.2).

[23] We performed scanning electron microscopy (SEM) imaging of some of these ion probe spots characterized by anomalously high Li signals. Results unambiguously show the presence of aluminosilicate grains within the “anomalous” spots. As shown in Figure 4, the silicate grains are generally about 1–3  $\mu\text{m}$  in diameter and are embedded within the calcite matrix, in contrast to the micrograins located in the coated zone and in chambers. We found no evidence of smaller silicate grains inside the pores located at depth and exposed by the spots (Figure 4). Migration of silicate micrograins from surface to deep pores during diagenetic processes seems unlikely in this case. In order to make a direct link between these Al-Si grains and Li contents, ion imaging was performed using the ims 1270 ion microprobe. The results are striking, since elevated Li contents are systematically associated with the presence of Al-Si grains, as shown in Figure 5. Image treatment allows us to roughly estimate Al/Si ratios for some of these grains (Al/Si~1), suggesting the presence of clay minerals. Unfortunately, these grains are too small for performing  $^7\text{Li}/^6\text{Li}$  in situ measurements, using



**Figure 4.** Example of a SEM X-ray map of a spot previously excavated by ion microprobe in the calcite part of a *Globigerinoides* test. Silica is also shown for the same spot and highlights the presence of micron-sized silicate grains, also rich in aluminum (not shown here), clearly incorporated within the calcite matrix. No grain is found in the pores located at depth and exposed by the sputtering. Scale bars are 12  $\mu\text{m}$ .



**Figure 5.** Example of Li-Al-Si maps performed using the 1270 ion microprobe within spots induced by previous in situ Li isotope measurements for Serie B foraminifera. In all maps, high Li signals are found to be systematically associated with high Si and Al signal. For clarity, the measured intensities have been normalized in order that the range of colors is 0–256 for all considered elements. The squares are  $20 \times 20 \mu\text{m}$ .

the same technique. It is also difficult to envisage cleaning or grinding techniques to separate these grains from the other grains located in the coated area or in the chamber cavities. By contrast, thirty Li intensity analyses of one hundred cycles each were performed in modern corals from New Caledonia ( $166^{\circ}3\text{E } 22^{\circ}3\text{S}$ ) and show very homogeneous Li contents (Figure 3), with no increase of Li intensity during the course of the run. The coral aragonite matrix does not contain detectable aluminosilicate micrograins.

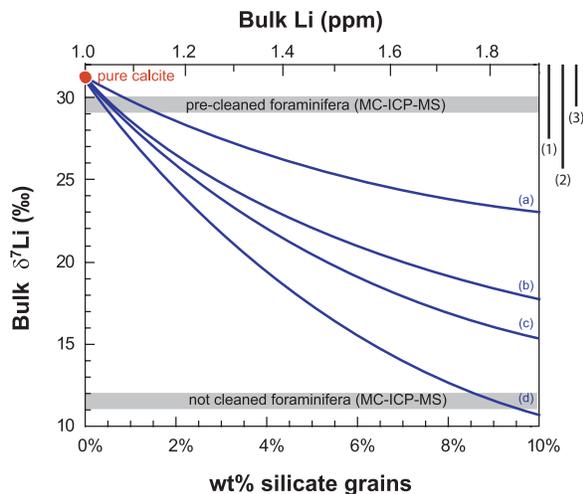
#### 4. Discussion and Conclusion

[24] Al-Si micron-sized grains in the calcite matrix or in deep pores of foraminifera are a serious

limitation to in situ analyses since they can be numerous in some tests. Indeed, we roughly estimated that  $\sim 75\%$  of the in situ analyses were affected by these grains. However, isotopic measurements could be performed in a few tests of *Globigerinoides* and *Gr. inflata* by using the variations of Li intensity to filter the data (Serie A, Table S2), as has been previously performed for ion microprobe Sr and Mg measurements [Allison and Austin, 2003].

[25] It is likely that these grains, enriched in Li, will affect isotopic analyses performed on a batch of bulk foraminifera, by using MC-ICP-MS or TIMS techniques. Broecker and Clark [2003] considered that about  $7 \pm 3\%$  of silicate grains can still be associated with the foraminifera after a standard grinding and precleaning procedure. Our data allow us to quantify the bias in  $\delta^7\text{Li}$  associated with a few percent of silicate grains remaining after the pre-cleaning process. Figure 6 shows that presuming Al-Si grains have a  $\delta^7\text{Li}$  typical of clays formed during oceanic crust low-temperature weathering ( $15\%$  [Chan et al., 1992]) and a Li content of 10 ppm, the presence of 2 wt% of residual silicate grains in the calcite matrix will lower the  $\delta^7\text{Li}$  of the bulk foraminifera by about 3‰. If the Li content of the clays is 70 ppm [Chan et al., 2006], then only 0.3 wt% of residual clay is required to lower  $\delta^7\text{Li}$  by 3‰. Alternatively, a 2wt% of residual clay will lower  $\delta^7\text{Li}$  by 10‰.

[26] The presence of embedded Al-Si grains within the foraminifera calcite therefore seems critical since it has been shown that ocean  $\delta^7\text{Li}$  has not varied by more than a few per mil in the last 18 Myr [Hathorne and James, 2006]. A single batch of foraminifera has been analyzed pre-cleaned and not pre-cleaned (Table S3). Comparison between both batches confirms that the amount of contaminant Li removed by the cleaning procedure is significant ( $\sim 80\%$ ). Major and trace element analyses in the leachates obtained during the cleaning procedure highlight correlations between Li and Al and Si (not shown here), strongly suggesting that the main Li contaminant for these foraminifera is of silicate origin. When not pre-cleaned, the  $\delta^7\text{Li}$  value was much lower ( $11.5\%$ ), suggesting that  $\delta^7\text{Li}$  for noncalcite lithium is significantly lower than  $11\%$ . It can be roughly calculated that for this sample, the contaminant Li has a  $\delta^7\text{Li}$  value of  $-2.4\%$ . Mixing calculations were therefore also done (Figure 6) by considering that  $\delta^7\text{Li}$  for the contaminant end-member is equal to  $4\%$  (MORB [Chan and Edmond, 1988]),  $-1\%$  (clastic marine



**Figure 6.** Theoretical curves defining a mixture between a calcite end-member of seawater composition (31.2‰) and several silicate end-members representing typical materials found in the ocean: curve a, low-T clay with  $\delta^7\text{Li} = 15\text{‰}$  and  $\text{Li} = 10$  ppm; curve b, fresh MORB with  $\delta^7\text{Li} = 4\text{‰}$  and  $\text{Li} = 10$  ppm; curve c, clastic marine sediment with  $\delta^7\text{Li} = -1\text{‰}$  and  $\text{Li} = 10$  ppm; curve d, serpentine mineral  $\delta^7\text{Li} = -10\text{‰}$  and  $\text{Li} = 10$  ppm. Curve a shows that contamination with 2% of a typical oceanic clay can decrease the foraminifera  $\delta^7\text{Li}$  down to 28‰. For comparison, we also show the MC-ICP-MS measurements for precleaned and not precleaned batches of planktonic foraminifera (see Table S3), as well as the range of  $\delta^7\text{Li}$  values obtained for planktonic species of foraminifera (1) from Hall *et al.* [2005], (2) from Hathorne and James [2006], and (3) from this study (Table S3).

sediments [Tomascak, 2004]) and  $-10\text{‰}$  (serpentine minerals [Decitre *et al.*, 2002]). These simple calculations illustrate the effect of the incorporated lithium, and the difficulty when estimating  $\delta^7\text{Li}$  based on bulk foraminifera dissolution. As a consequence, this effect may explain, at least partially, the observed discrepancy between published data.

[27] The presence of silicate grains incorporated within the calcite matrix, as exemplified in Figure 4, is a priori surprising. Assimilation of silicate grains by foraminifera is generally thought to occur after deposition on the seafloor, in the easily accessible pores and chamber cavities. Yet, it is difficult to envisage migration of micron-sized grains within an already precipitated calcite matrix, although this possibility cannot be excluded. On the other hand, the presence of these small grains inside the foraminifera walls is consistent with the biomineralization model of Erez [2003]. In this model, the biomineralization process is based on seawater vacuolization. During their growth, fora-

minifera “catch” seawater vacuoles from which calcite precipitates. In this scenario, it is likely that small silicate grains present in the surrounding seawater might be directly transferred by the vacuoles to the foraminifera, and then deposited along with the newly precipitated calcite. By contrast, biomineralization models of corals do not a priori invoke an uptake of seawater vacuoles (see Cohen and McConnaughey [2003] for a review). Calcium carbonate in corals is instead precipitated from ions in solutions which have passed through several membranes and pumps, and therefore it seems less likely that micrograins could reach the calcification sites. It seems consistent with the proposed biomineralization mechanisms that corals do not contain detectable Al-Si micrograins in contrast to foraminifera, as is strongly suggested by homogeneous Li content found for the analyzed corals. However, more data are needed in order to better explore and compare both biomineralization processes.

[28] Ion microprobe in situ  $\delta^7\text{Li}$  measurements in biogenic calcite and aragonite matrices offer a new possibility of investigating both biomineralization processes and the past record of the ocean composition, by exploring geochemical variations at a scale that is smaller in space and in time. It also represents a specific means of avoiding the non-calcitic lithium present in and around foraminiferal tests.

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## References

Aléon, J., M. Chaussidon, M. Champenois, and D. Mangin (2001), Quantitative imaging of stable isotopes by ion microprobe, *Geostand. Newslett.*, 25, 417–429.

- Allison, N., and W. E. N. Austin (2003), The potential of ion microprobe analysis in detecting geochemical variations across individual foraminifera tests, *Geochem. Geophys. Geosyst.*, 4(2), 8403, doi:10.1029/2002GC000430.
- Beck, P., J. A. Barrat, M. Chaussidon, P. Gillet, and M. Bohn (2004), Lithium isotopes in the northwest Africa 480 shergottite (NWA 480): A record of degassing of Martian magmas?, *Geochim. Cosmochim. Acta*, 68, 2925–2933.
- Beck, P., M. Chaussidon, J. A. Barrat, P. Gillet, and M. Bohn (2006), Diffusion induced Li isotopic fractionation during the cooling of magmatic rocks: The case of pyroxene phenocrysts from nakhlite meteorites, *Geochim. Cosmochim. Acta*, 70, 4813–4825.
- Broecker, W. S., and E. Clark (2003), Role of sonification in shell weight measurements, *Geochem. Geophys. Geosyst.*, 4(11), 1093, doi:10.1029/2003GC000569.
- Brown, S. J., and H. Elderfield (1996), Variations in Mg/Ca and Sr/Ca ratios of planktonic foraminifera caused by post-depositional dissolution: Evidence of shallow Mg-dependence dissolution, *Paleoceanography*, 11(5), 543–551.
- Carignan, J., D. Cardinal, A. Eisenhauer, A. Galy, M. Rehkämper, F. Wombacher, and N. Vigier (2004), A reflection on Mg, Cd, Ca, Li and Si isotopic measurements and related materials, *Geostand. Geoanal. Res.*, 28, 139–148.
- Chan, L. H., and J. M. Edmond (1988), Variation of lithium isotope composition in the marine environment: A preliminary report, *Geochim. Cosmochim. Acta*, 52, 1711–1717.
- Chan, L.-H., J. M. Edmond, G. Thompson, and K. Gillis (1992), Lithium isotopic composition of submarine basalts: Implications for the lithium cycle in the oceans, *Earth Planet. Sci. Lett.*, 108, 151–160.
- Chan, L.-H., J. C. Alt, and D. A. H. Teagle (2002), Lithium and lithium isotope profiles through the upper oceanic crust: A study of seawater–basalt exchange at ODP sites 504B and 896A, *Earth Planet. Sci. Lett.*, 201, 187–201.
- Chan, L.-H., W. P. Leeman, and T. Plank (2006), Lithium isotopic composition of marine sediments, *Geochem. Geophys. Geosyst.*, 7, Q06005, doi:10.1029/2005GC001202.
- Chaussidon, M., and F. Robert (1998),  $^7\text{Li}/^6\text{Li}$  and  $^{11}\text{B}/^{10}\text{B}$  variations in chondrules from the Semarkona unequilibrated chondrite, *Earth Planet. Sci. Lett.*, 164, 577–589.
- Cohen, A. L., and T. A. McConnaughey (2003), Geochemical perspectives on coral mineralization, in *Biom mineralization*, *Rev. Mineral. Geochem.*, vol. 54, edited by P. M. Dove, J. J. De Yoreo, and S. Weiner, pp. 151–187, Mineral. Soc. of Am., Washington, D. C.
- Decitre, S., E. Deloule, L. Reisberg, R. James, P. Agrinier, and C. Mével (2002), Behavior of Li and its isotopes during serpentinization of oceanic peridotites, *Geochem. Geophys. Geosyst.*, 3(1), 1007, doi:10.1029/2001GC000178.
- Deloule, E., M. Chaussidon, and P. Alle (1992), Instrumental limitations for isotope measurements with a Caméca<sup>®</sup> ims-3f ion microprobe: Example of H, B, S and Sr, *Chem. Geol.*, 101, 187–192.
- Erez, J. (2003), The sources of ions for biomineralisation in foraminifera and their implications for paleoceanographic proxies, in *Rev. Mineral. Geochem.*, vol. 54, edited by P. M. Dove, J. J. De Yoreo, and S. Weiner, pp. 115–149, Mineral. Soc. of Am., Washington, D. C.
- Hall, J. M., and L.-H. Chan (2004), Li/Ca in multiple species of benthic and planktonic foraminifera: Thermocline, latitudinal, and glacial-interglacial variation, *Geochim. Cosmochim. Acta*, 68, 529–545.
- Hall, J. M., L.-H. Chan, W. F. McDonough, and K. K. Turekian (2005), Determination of the lithium isotopic composition of planktic foraminifera and its application as a paleo-seawater proxy, *Mar. Geol.*, 217, 255–265.
- Hathorne, E. C., and R. H. James (2006), Temporal record of lithium in seawater: A tracer for silicate weathering?, *Earth Planet. Sci. Lett.*, 246, 393–406.
- Hathorne, E. C., O. Alard, R. H. James, and N. W. Rogers (2003), Determination of intratest variability of trace elements in foraminifera by laser ablation inductively coupled plasma-mass spectrometry, *Geochem. Geophys. Geosyst.*, 4(12), 8408, doi:10.1029/2003GC000539.
- Hoefs, J., and M. Sywall (1997), Lithium isotope composition of Quaternary and Tertiary biogenic carbonates and a global lithium isotope balance, *Geochim. Cosmochim. Acta*, 61, 2679–2690.
- Huh, Y., L.-H. Chan, L. Zhang, and J. M. Edmond (1998), Lithium and its isotopes in major world rivers: Implications for weathering and the oceanic budget, *Geochim. Cosmochim. Acta*, 62, 2039–2051.
- Kosler, J., M. Kucera, and P. Sylvester (2001), Precise measurement of Li isotopes in planktonic foraminiferal tests by quadrupole ICPMS, *Chem. Geol.*, 181, 169–179.
- Marriott, C. S., G. M. Henderson, N. S. Belshaw, and A. W. Tudhope (2004a), Temperature dependence of  $\delta^7\text{Li}$ ,  $\delta^{44}\text{Ca}$  and Li/Ca incorporation into calcium carbonate, *Earth Planet. Sci. Lett.*, 222, 615–624.
- Marriott, C. S., G. M. Henderson, R. Crompton, M. Staubwasser, and S. Shaw (2004b), Effect of mineralogy, salinity, and temperature on Li/Ca and Li isotope composition of calcium carbonate, *Chem. Geol.*, 212, 5–15.
- Millot, R., C. Guerrot, and N. Vigier (2004), Accurate and high-precision measurement of lithium isotopes in two reference materials by MC-ICP-MS, *Geostand. Geoanal. Res.*, 28, 153–159.
- Qi, H. P., P. D. P. Taylor, M. Berglund, and P. De Bièvre (1997), Calibrated measurements of the isotopic composition and atomic weight of the natural Li isotopic reference material IRMM-016, *Int. J. Mass Spectrom. Ion Processes*, 171, 263–268.
- Rollion-Bard, C., M. Chaussidon, and C. France-Lanord (2003), pH control on oxygen isotopic composition of symbiotic corals, *Earth Planet. Sci. Lett.*, 215, 275–288.
- Tomascak, P. B. (2004), Developments in the understanding and application of lithium isotopes in the earth and planetary sciences, in *Geochemistry of Non-traditional Stable Isotopes*, *Rev. Mineral. Geochem.*, vol. 55, edited by C. M. Johnson, B. L. Beard, and F. Albarede, pp. 153–195, Mineral. Soc. of Am., Washington, D. C.
- You, C.-F., and L.-H. Chan (1996), Precise determination of lithium isotopic composition in low concentration natural samples, *Geochim. Cosmochim. Acta*, 60, 909–915.