Supplementary Material - JAAS Paper Ref. B907122A

A. Sample analyses and precision calculation:

Sample analysis by Q-ICP-MS was done following standard-sample-standard bracketing protocol. A total of five such replications were done for a single column eluted sample. The δ^7Li of each replicate (individual analysis) was calculated using the following equation;

$$\delta^7 Li(‰) = \left\{ \left[\frac{\left(\frac{^7Li}{^6Li}\right)_{\text{Sample}}}{\left(\frac{^7Li}{^6Li}\right)_{\text{Standard}-\text{average}}} \right] - 1 \right\} \times 1000$$

Where, $\left(\frac{^7Li}{^6Li}\right)_{\text{Standard}-\text{average}}$ = Average $\left(\frac{^7Li}{^6Li}\right)_{\text{Count ratio}}$ of L-SVEC Li standard run before and after each sample analysis.

The 2σ uncertainty for samples were calculated using the following equation;

$$\sigma = \sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}}$$

Where n = 5, x is the δ^7Li value of an individual analysis, and $\bar{x}$ is the mean of five analyses.

B. Matrix Na tolerance - δ^7Li (‰) of Na doped L-SVEC Li standards in 2% HNO_3

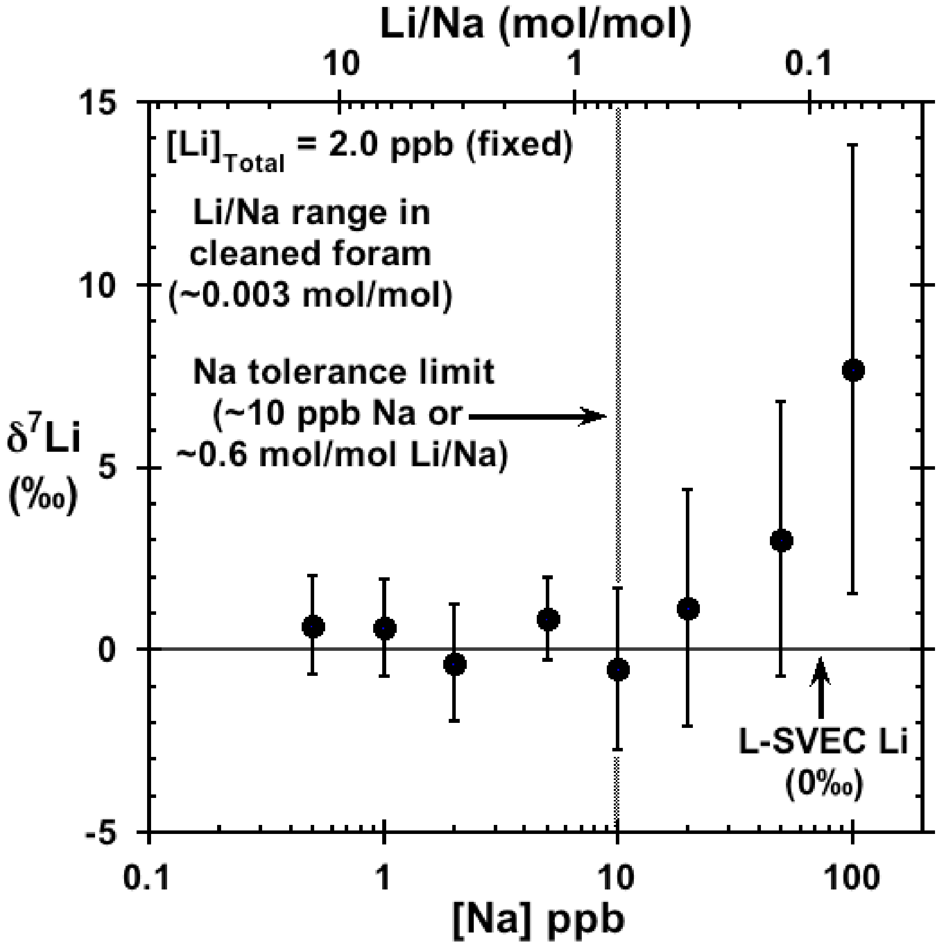

Figure B. Lithium isotope ratios of L-SVEC Li standard ([Li] = 2 ppb, fixed) doped with increasing concentration of sodium (0.5 ppb to 100 ppb). Li/Na ratios (mol/mol) are plotted on the top Y-axis. The samples were analyzed using standard-sample-standard bracketing technique. Each symbol represents an average of five separate analyses with 2σ external variation. The Na tolerance limit of the Q-ICP-MS for matrix-based sodium determined in this study is relatively high (> 0.6 mol/mol, Li/Na). Moreover, tolerance limit of this ICP-MS method for total matrix sodium (10 ppb, Na) is well within the cumulative sodium blank from our chromatographic separation method (see text).

C. Matrix Ca tolerance - δ^7Li (‰) of Ca doped L-SVEC Li standards in 2% HNO_3

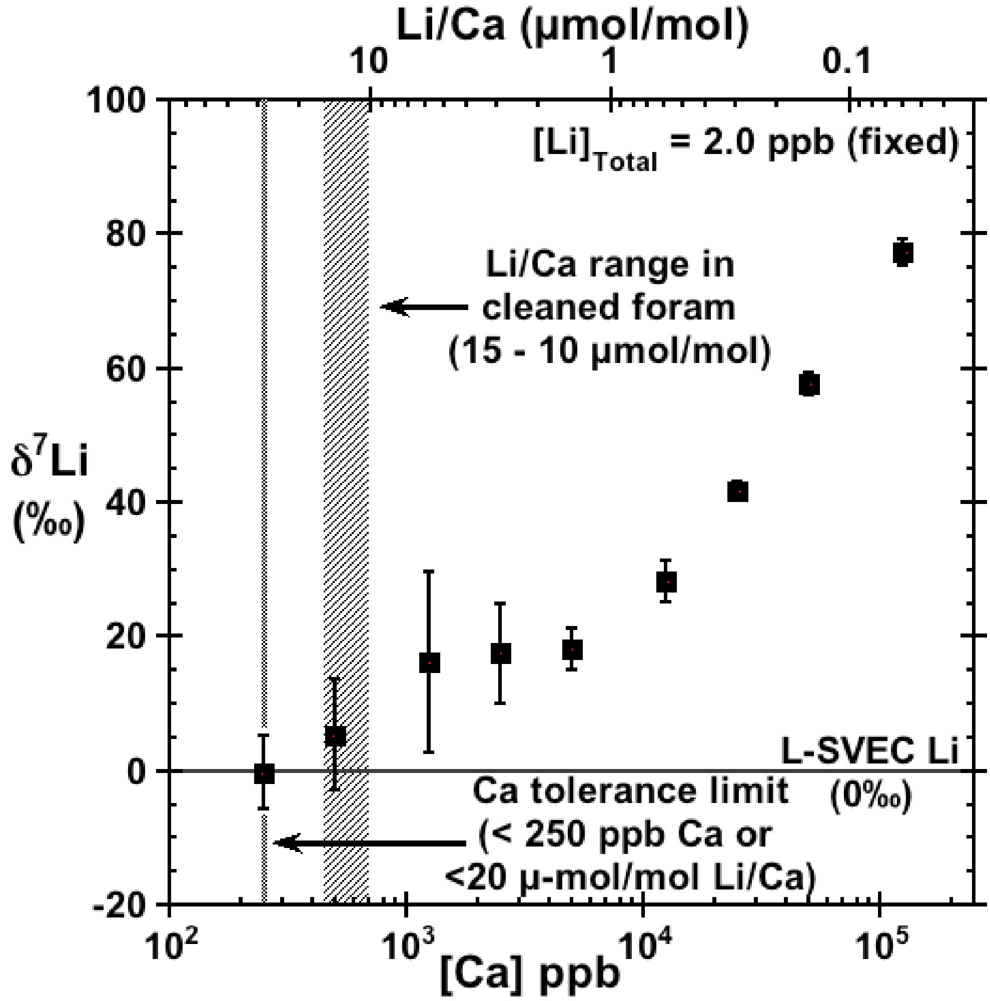

Figure C. Lithium isotope ratios of L-SVEC standard ([Li] = 2 ppb, fixed) doped with increasing concentration of calcium (250 ppb to $125\text{x}10^3$ ppb). Li/Ca ratios (μmol/mol) are plotted on the top Y-axis. The samples were analyzed using standard-sample-standard bracketing technique. Each symbol represents an average of five separate analyses with 2σ external error. The tolerance limit of the Q-ICP-MS for matrix-based calcium determined in this study is relatively high (~20 μmol/mol, Li/Ca). Moreover, tolerance limit of this ICP-MS method for total matrix calcium (250 ppb, Ca) is well within the cumulative calcium blank from our chromatographic separation method (see text).

D. Dead-time correction:

Normally, for an Agilent 7500cs mass spectrometer, the detector dead-time is calibrated using In (indium, m/z = 115) or Er (erbium, m/z = 166) as the standard reference mass. The default dead-time value for reference mass 166 amu is 38 ns. However, the dead-time value of the entire mass spectrum (0 amu to 260 amu) can range from about 30 ns to 60 ns depending on detector age. The Agilent operating system uses a mass dependent (6.0 ns/ 260 amu) correction factor to determine the exact dead-time for other masses by applying a simple linear equation.

If the dead-time at reference mass (166 amu) is $\text{D-T}_{166\text{ amu}}$ ns then the dead time at mass M amu ($\text{D-T}_{\text{M amu}}$) is given by;

$$\text{D-T}_{\text{M amu}}\text{ (ns)} = \text{D-T}_{166\text{ amu}}\text{ (ns)} + [(6\text{ ns}) \times (\text{M amu} - 166\text{ amu})/260\text{ amu}]$$

Where, 6 ns/ 260 amu is the correction factor (CF). The correction factor is determined experimentally and is fixed for all Agilent 7500 series mass spectrometers. The mass dependency of the dead-time correction is due to non-linearity of pulse mode detection and detector baseline shift from the discriminator baseline at high ion count rates. By performing our dead-time calibration directly on 6 amu and 7 amu (^{6}Li and ^{7}Li) the mass dependency in dead-time calculation is avoided. Moreover, at 1 amu mass difference the dead-time variation between 6 amu and 7 amu is approximately 0.023 ns (6 ns/ 260 amu), which is insignificant (<0.01%) in comparison to the actual dead-time (~36 ns).