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 $\delta^7$Li of each replicate (individual analysis) was calculated using the following equation:

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

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

The $2\sigma$ 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 $\delta^7$Li value of an individual analysis, and $\bar{x}$ is the mean of five analyses.
B. Matrix Na tolerance - $\delta^7\text{Li}$ (‰) 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 - $\delta^7$Li (‰) 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 125x10$^3$ 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 D-T_{166\text{ amu}} ns then the dead time at mass M amu (D-T_{M\text{ amu}}) is given by;

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

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\text{Li} and ^7\text{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).