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Li isotopic measurements: preparation and characterization of secondary reference materials and applications to hydrochemistry and weathering

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Although a significant improvement of the analytical precision of Li isotopic measurements with the use of new generation TIMS and MC-ICP-MS, there are still accuracy problems on available geological reference materials. Indeed, whereas there is a general agreement between laboratories for the sea water Li isotopic composition, reported values for rock samples may vary well outside the assigned uncertainty from one laboratory to another. For example, $\delta^7 \text{Li}_{L-SVEC}$ reported for the JB-2 basalt vary from 3.9±0.9 permil to 6.8±0.3 permil, which may result from either isotopic heterogeneity of the material, chemical treatments prior to analysis problems or analytical and data treatment problems. We have prepared at CRPG secondary reference materials by mixing ⁷Li and ⁶Li spikes with either L-SVEC or IRMM 016 samples to produce solutions having a known Li concentration and isotopic composition. The 7Li-N and 6Li-N solution samples have nominal isotopic composition of 30.1 permil and -9.7 permil respectively relative to L-SVEC and concentrations of 100 mg/L. Repeated measurements of these samples using the ICP-MS at CRPG yielded 30.1 ± 1.0 permil (n=8) and -8.8±0.6 permil (n=9) at 2 sigma level of confidence (2*standard deviation). An additional LiCl-N solution was measured and yielded a delta value of 9.5±0.5 permil (n=4). Identical results were obtained at the BRGM from analyses performed with the Neptune MC-ICP-MS (30.1±0.3 permil, n=43 and 9.7±0.3 permil, n=7 for the 7Li-N and LiCl-N samples respectively). These secondary reference materials, previously passed through ion exchange resin or directly analysed, will be used for checking the accuracy of Li isotopic measurements over a range of almost 40 permil and will be available to the scientific community.

Because of their large relative mass difference and therefore fractionation, lithium iso-

topes have been studied for several years to trace both sources and physico-chemical processes affecting various geological samples and environments. Indeed, these studies shown that dissolved and particulate Li in rivers have $\delta^7 \text{Li}_{L-SVEC}$ from 6 permil to 32 permil which, in some cases, may be related to some weathering parameters. Correlation with Li concentration is not straightforward although dissolved Li and Mg concentrations seem to be related suggesting possible common sources. We have studied the composition of dissolved element in the Moselle river and tributaries, NE France, for which the draining basin is highly contrasted in lithology: silicate rocks upstream and mostly chemical sediments (carbonate-evaporite) downstream. We show that Li and Mg concentrations are well correlated in all samples but water draining carbonate-evaporite rocks define a steeper slope than water draining silicate rocks, suggesting different sources and/or weathering processes. Furthermore, tributaries draining exclusively carbonate-evaporite rocks have extremely high Li concentration of up to 60 microgram/L compared to 0.5 – 2.8 microgram/L for water draining exclusively silicate rocks. The Li isotopic composition of these contrasted river waters will be presented.