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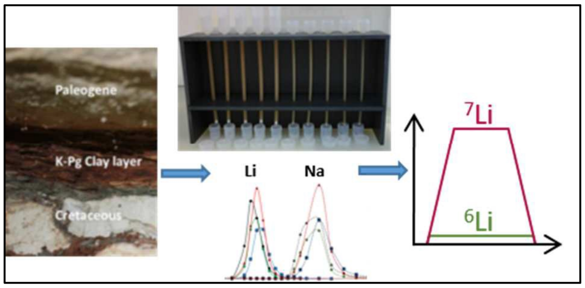
Graphical abstract



10-20 words

An ion chromatographic procedure allows isolation of lithium from carbonate and clay material prior to isotope ratio determination with MC-ICP-MS.

Single-step chromatographic isolation of lithium from whole-rock carbonate and clay for isotopic analysis with multi-collector ICP-mass spectrometry

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Abstract

Lithium isotope ratios play a key role in tracing weathering processes within the context of paleoclimatologic research. Therefore, accurate and precise determination of the isotopic composition of Li is required for a large variety of complex geological samples with widely different Li contents. This technical note describes the extension and fine-tuning of the existing cation exchange chromatographic procedures for isolation of Li to whole-rock carbonate and clay matrices prior to its isotopic analysis via multi-collector ICP-mass spectrometry. The method developed permits the isolation of ≥ 20 ng amounts of Li from carbonates and clays, by using a 25 cm long cylindrical column loaded with 8 and 2 mL of AG-50W-X8 cation exchange resin, respectively. A 0.5 M HCl solution is used as eluent. Li recoveries ≥ 99 % were achieved and isotopic analysis using 10-20 ng of isolated Li resulted in accurate and precise δ^7Li values – external precision (2SE) of 0.2 ‰ (N=15). The analytical procedures developed allow Li isotope ratios to be investigated in parallel in both the clay and carbonate fractions of a geological sample within the context of paleoclimatological research.

Keywords

Li isotope ratio, MC-ICP-MS, clay, carbonate

Introduction

Li has two stable isotopes, ^6Li and ^7Li, with an average terrestrial relative abundance of 7.59 % and 92.41 %, respectively [1]. As Li is one of the lightest elements, fractionation between its two stable isotopes is prevalent in nature, giving rise to a relative large natural variation in the $^7Li/^6Li$ isotope ratio. With respect to the Li_2CO_3 isotopic reference material L-SVEC (δ^7Li of 0.0 ‰), δ^7Li values range between +56.3 ‰ in pore water and -12.6 ‰ in silicates [2-4]. The large difference between these δ^7Li values illustrates an important cause of Li isotope fractionation, as the light isotope ^6Li is preferentially retained within the solid phase during primary clay mineral dissolution and secondary clay mineral formation, while the heavier isotope ^7Li is enriched in the liquid phase [5]. Li isotope ratios hence act as a tracer for water/rock interactions, such as continental weathering and recycling of oceanic crust [5-9]. During continental weathering, the formation of secondary clays induces large Li isotope fractionation, causing marked variations in the Li isotopic composition of the ocean throughout geological time. Contrary, marine carbonates incorporate this seawater δ^7Li signature into the $CaCO_3$ lattice without isotope fractionation, providing a direct window onto past climatic events [10-11]. Measuring the Li isotopic composition in parallel in both the clay and the carbonate fractions isolated from whole-rock hemipelagic limestones, provides the potential to study this coupled behavior, which so far is underexplored in paleoclimatologic research.

Such studies require highly precise and accurate determination of Li isotope ratios in both components, which are geochemically very different from one another, both in matrix composition and in natural Li content. Multi-collector ICP-mass spectrometry (MC-ICP-MS) is suited for highly precise and accurate isotopic analysis of Li, provided that purified sample solutions with a sufficiently high target element concentration and free from matrix components are introduced.

In order to obtain a sufficient sample volume with a concentration suitable for MC-ICP-MS analysis 10-20 ng of Li is necessary. Particularly samples characterized by a heavy matrix and a Li concentration <1 µg/g, such as whole-rock carbonates, present specific challenges, as for an expected Li concentration ~ 0.1 µg/g at least 100 mg of carbonate needs to be processed in a robust ion exchange chromatographic procedure. Thereby, the effect of on-column isotope fractionation of Li during its isolation from the matrix needs to be avoided by aiming at quantitative recovery [12]. Separation of Li from Na is the crucial step in the isolation procedure, as (1) Na is a major element of carbonate and clay material and (2) distribution coefficients, representing the ratio of equilibrium concentration of each cation in the stationary phase (cation exchange resin) to that in the mobile phase, are very similar for Li and Na [13]. Several one-column procedures for this purpose relying on the use of AG50W-X8 cation exchange resin have been described in literature. Mineral acids with [5, 14-16] or without [12] an admixed organic solvent are used as eluent. The procedure developed by Misra and Froelich [12] is suitable for a maximum of 1 to 2 mg of calcium carbonate, containing 1 to 2 ng of Li, only. In this work, we provide a complete method (i) to separate the clay and carbonate fractions from whole-rock carbonate from one another, (ii) to upscale the chromatographic isolation procedure for both the clay and carbonate fractions and (iii) to determine Li isotope ratios in parallel in both components of whole-rock hemipelagic limestones. This method is the result of an optimization of the sample preparation and ion exchange chromatography procedures, including evaluation of the effect of the concentration of the acid used to dissolve the whole-rock carbonate, of the resin volume and of the column cation load. Parameters assessed were the elution volumes of Li^+ and Na^+, the completeness of the separation of Li^+ from Na^+, the Li recovery, Li isotope ratio results, and the resin pretreatment required to minimize concentrations of Li and Na in the procedural blanks. In addition, MC-ICP-MS data acquisition parameters and the Li concentration in the final sample solutions were optimized in view of an efficient use of the amount of Li available for accurate and precise determination of the Li isotope ratio. In this way, a parallel investigation of Li isotope ratios in both the clay and the carbonate fraction of hemipelagic limestones allows the coupled behavior of Li in the context of paleoclimatologic research to be explored. The method described here was subsequently adopted to bulk hemipelagic limestones across two Cretaceous-Paleogene (K-Pg) boundary sections (Furlo Pietralata and Fonte d'Olio), sampled at high-resolution, and to a separate clay fraction (Petriccio) in the Umbria-Marche region, Central Italy. The in-depth interpretation of the corresponding results is presented elsewhere [17]. In addition, the optimized method is suitable for studying variation of Li isotope ratios in other carbonate materials, such as speleothems.

Materials and methods

Chemicals and materials

Ultra-pure Optima® HCl was purchased from Fisher (Acros Organics, Belgium). The acid concentration of each batch was accurately determined by acid-base titration with NaOH and phenolphthalein as an indicator. In turn, oxalic acid was used as a titrant to determine the exact concentration of the NaOH solution. Pro analysis grade 14 M HNO_3 (Chem-Lab, Belgium) was further purified by sub-boiling distillation in PFA equipment. Dilutions were prepared using ultrapure water with ≥18.2 MΩ.cm resistivity, provided by a Milli-Q Element unit (Millipore, France). Ethanol p.a. was purchased from Sigma Aldrich (Belgium). Finally, single-element 1 g/L standard solutions of Li, Be, Na, Ca, Mg, Sc, Sr and Y were obtained from Inorganic Ventures (VI, USA). Li carbonate isotopic reference material IRMM-016 (IRMM, Belgium) was used in standard solutions, deployed for evaluation of the isolation procedure and for calibration of Li isotopic analysis.

For optimization of the isolation of Li from carbonate, both the certified reference material NIST SRM 915 calcium carbonate (National Institute for Standards and Technology NIST, MD, USA) and whole-rock carbonate from the K-Pg pelagic limestones from Fonte d'Olio (FDO) in Umbria-Marche (Italy), sampled at a depth of 30 cm below the K-Pg boundary, were used. Carbonate samples of 150 mg each were dissolved in 12 mL of 0.28 M HCl or 7 mL of 0.50 M HCl and the digest thus obtained was subsequently centrifuged in order to pellet and remove any silicate material present in the solution. The supernatant was subsequently transferred to clean Savillex® beakers. These low acid concentrations and thus, large sample volumes, were necessary to prevent leaching of Li from the clay fraction into the dissolved carbonate fraction [18].

Clay samples were isolated from whole-rock carbonate originating from the K-Pg pelagic limestones from Furlo Pietralata (FPL) and Fonte d'Olio (FDO) in Umbria-Marche (Italy). For that purpose, the carbonate was dissolved in sodium acetate buffer solution (pH = 5) and the remaining clay fraction was dried and subsequently acid-digested. Ten mg aliquots of dried clay with a Li content of 60-80 µg/g were weighed in 15 mL Savillex® beakers and digested in two steps. In the first step, 6 mL of HF + 2 mL of HNO_3 were used and in the second step, 8 mL of *aqua regia*. Both digestions were performed at 110 °C for 48 h. The digests thus obtained were evaporated to dryness at 80 °C. Finally, the residue obtained was taken up in 0.8 mL of 0.22 M HCl. All sample handling, except for centrifugation and weighing, was carried out in a class-10 clean lab.

Chromatographic isolation of Li was established using AG 50W-X8 cation exchange resin with 100–200 µm mesh size (Biorad, Belgium), packed into Savillex® microcolumns with an internal diameter of 3.2, 4.0 or 6.4 mm and a column length of 25 cm. The respective resin volumes used were 2.0, 3.0 and 8.0 mL, corresponding to a cation exchange capacity of 3.4, 5.1 and 13.6 meq, respectively.

ICP-MS instrumentation

Elemental assays were performed with a Thermo Scientific XSeries II quadrupole-based ICP-MS instrument (Germany), equipped with a 1 mL/min concentric nebulizer, mounted onto a quartz impact bead spray chamber cooled to 1 °C. Sample solution was introduced at a rate of 0.5 mL/min via a peristaltic pump. **Table 1** presents the instrument settings and data acquisition parameters. Nuclides monitored were ^{7}Li, ^{9}Be, ^{23}Na, ^{24}Mg, ^{25}Mg, ^{44}Ca, ^{45}Sc, ^{56}Fe, ^{86}Sr, ^{88}Sr, ^{89}Y. Iron was determined in CCT operation mode with He/H_2 as a collision-reaction gas at a flow rate of 5.1 mL/min. Additionally, kinetic energy discrimination with a decelerating potential of 3 V was applied between hexapole and quadrupole.

A Thermo Scientific Neptune MC-ICP-MS instrument was used for determination of Li isotope ratios. Sample introduction was accomplished using a peristaltic pump connected to a 50 µL/min PFA concentric nebulizer, mounted onto a quartz dual spray chamber. External correction in a sample-standard bracketing approach was relied on for the correction for instrumental mass discrimination, with the same Li concentration in the standard and all sample solutions, varying between 10 and 50 µg/L throughout all experiments. **Table 1** presents the instrument settings and data acquisition parameters used.

Optimization of Li isotopic analysis via MC-ICP-MS

In order to minimize the analysis time and hence, the required mass of Li for its isotopic analysis via MC-ICP-MS, a series of 8 experiments each consisting of 11 sequential measurements of

IRMM-016 standard in 0.28 M HNO_3 was performed. Evaluated responses were average δ^7Li and precision (2s) of 9 determinations. The concentration of Li (10, 25, 40 or 50 µg/l), the number of replicate measurements (10 *versus* 15) and the integration time per measurement (2.1 *versus* 4.2 s) were varied in these experiments. **Table 2** summarizes the experimental approach. For isotope ratio determination in the final samples, an integration time of 2.1 s and a Li concentration of 25 or 50 µg/L were used and the result was based on 10 successive measurements (see also **Table 1**).

Optimization of the isolation of Li from carbonate and clay matrices

A general protocol for the preparation of microcolumns for Li isolation via cation exchange chromatography and their subsequent use is shown in **Table 3**, as well as a summary of the conditions used during the optimization study.

Optimization of the method for the isolation of Li from carbonate matrices was carried out using a synthetic $CaCO_3$ standard, which was matrix-matched to whole-rock carbonate by dissolving $CaCO_3$ NIST SRM 915 reference material and spiking the solution thus obtained with Li (1 µg/g), Na (300 µg/g), Sr (300 µg/g) and Mg (1500 µg/g) to match the typical concentrations in Cretaceous and Paleogene carbonates in the Umbria-Marche section, as determined via preliminary elemental analysis.

The experimental design included the parameters acid concentration of the sample solution loaded onto the column (0.28 *versus* 0.50 M HCl), the matrix cation load (10 *versus* 15 % of the total resin capacity) and the resin volume (3 mL *versus* 8 mL). It was investigated which of the separately collected 0.50 M HCl eluent fractions contained Li^+ and Na^+, while the respective recoveries of both elements were quantified. **Table 4** gives an overview of the experimental design used in this context. With 3 mL microcolumns, individual 1 or 2 mL eluent fractions were collected for analysis, while with the 8 mL columns, individual fractions of 2.5 or 5 mL were collected for this purpose.

From both sampling localities, a mixture of isolated and digested clay samples was prepared, *i.c.* a mixed sample from Furlo Pietralata (FPL) and one from Fonte d'Olio (FDO) was loaded onto 2 mL microcolumns with the aim of studying the isolation of Li from the clay matrix. Only the sample volume load (65 to 140 µl) was varied in the optimization study, as the cation load from the clay matrix was always lower than 1 % of the column capacity. The acid concentration of the digests was always 0.24 M HCl.

Individual 0.5-1.0 mL fractions were collected in 7 mL Savillex® beakers and evaporated to dryness overnight on a hotplate at 80 °C. Prior to elemental analysis, the residues were redissolved in 1.5 mL of 0.28 M HNO_3. Be, Sc and Y were added as internal standards at a concentration of 10 µg/L each. In all fractions, the Li, Na, Mg, Ca and Sr concentrations were determined using quadrupole-based ICP-MS (**Table 1**).

An additional experiment was performed in order to assess the Na^+ concentration as a function of the volume of 6 M HCl resin-cleaning solution flushed through the 3 and 8 mL columns prior to column conditioning (*cfr*. **Table 3**).

After successful optimization, Li was chromatographically isolated from both natural carbonate and clay samples and from synthetic samples spiked with Li isotopic standard. Natural carbonate fractions were dissolved in either 0.28 or 0.50 M HCl in order to evaluate the potential leaching of Li from the clay fraction into the dissolved carbonate fraction. During ion exchange chromatography experiments, the eluent fraction preceding the Li^+ elution peak, the eluent fraction containing Li^+ and the eluent fraction containing Na^+ were collected separately, evaporated to dryness and the residues redissolved in 0.28 M HNO_3 prior to analysis. The Li elution fraction was used for determination of the Li recovery and measurement of the corresponding isotope ratio. Isotope ratios were expressed using the delta notation, whereby δ^7Li is calculated according to **Eq. 1.** In this equation, $(^7\mathrm{Li}/^6\mathrm{Li})_s$ represents the isotope ratio (corrected for mass discrimination) in the sample and $(^7\mathrm{Li}/^6\mathrm{Li})_{std}$ refers to the certified isotope ratio of the bracketing standard, *i.e.* 12.177.

$$\delta\,^7\mathrm{Li}\,(‰) = \left(\frac{(^7\mathrm{Li}/\,^6\mathrm{Li})_s}{(^7\mathrm{Li}/\,^6\mathrm{Li})_{std}} - 1\right) \times 1000 \qquad \text{(Eq. 1)}$$

Results and discussion

Optimization of Li isotopic analysis using MC-ICP-MS

Variation of the Li concentration and the data acquisition parameters did not affect the average δ^7Li value obtained, which was 0.0 ‰ in all experiments. The internal precision (expressed as 2s for N = 9) ranged between 0.2 and 0.7 ‰, as indicated in **Table 2**. The influence of integration time and number of cycles and blocks on the precision was not reproducible within the ranges tested. However, it was clear that better precision and sensitivity was obtained for the higher concentrations. Consequently, a measurement consisting of 10 runs with a duration of 2.1 s each for isolates containing 25 to 50 µg/l Li was found adequate. Since 0.4 mL is deemed a minimal sample volume for proper sample introduction and measurement, a minimum Li mass of 10 to 20 ng is required. Further efforts to minimize the Li amount necessary hence should be focused on improval of sample introduction efficiency and sensitivity of the instrument.

Evaluation of 3 and 8 mL resin columns for Li isolation from carbonate samples

The elution profiles from all of the calibration experiments with 3 and 8 mL columns, listed in Table 4, are shown in **Figures 1** and **2**, respectively. With both column volumes, increasing the cation load from 10 to 15 % caused a shift of the Li^+ elution peak maximum towards smaller elution volumes. The 3 mL resin columns resulted in minor tailing of the Li^+ peak when loaded to 15 % of the resin capacity. Irrespective of sample load and volume, the chromatograms obtained using 3 mL columns showed a slight overlap between the Li^+ and Na^+ elution peaks. The total amount of Na in the Li elution fraction varied between 7 and 21 µg/l, giving rise to a Na/Li ratio between 2 and 8 for all 3 mL columns. In a separate experiment, 5000 µg/l of Na and a Na/Li ratio of 100 were assessed as the maximum allowable Na contamination not resulting in erroneous Li isotope ratios. Hence, the observed presence of Na in the isolated Li fractions was not expected to affect the accuracy of MC-ICP-MS analysis. The concentration of other matrix elements (Ca, Mg and Sr) in the Li fraction isolated using a 3 mL column were all below the LOD, *i.e.* <40, <3 and <0.2 µg/l, respectively.

Ion exchange chromatography experiments with 8 mL columns did not show tailing of the Li^+ elution peak, while complete separation of the Li^+ and Na^+ elution peaks was achieved. Despite the complete separation of these elution peaks, the sodium contamination was more severe, *i.e.* 100-150 µg/l, resulting in Na/Li ratios between 17 and 38. No Mg or Sr was detected, however up to 260 ng of Ca was found to co-elute with Na.

In order to identify the source of the Na contamination observed – either sample breakthrough or contamination from the resin or eluent – first the Na recovery in the Na^+ elution peak was quantified. As the Na^+ elution peak represented quantitative recovery of the Na present in the sample, sample breakthrough and loss of Na in the pre-elution fraction could be excluded. In a separate experiment, Na and Ca concentrations in subsequent column volumes of 6 M HCl resin-cleaning solutions, prior to sample load, were determined. This revealed high levels of Na contamination and significant Ca contamination as a result of these elements being washed from the resin. Three mL of resin released 78 µg of Na and 24 µg of Ca, while 8 mL of resin released 162 µg of Na and 51 µg of Ca in the first 4 column volumes of 6 M HCl resin-cleaning solution. It is clear that a minimum of 4 column volumes of 6 M HCl are necessary to sufficiently remove Na and Ca from the resin prior to its use for Li isolation (see **Figure S1** and **S2** in ESI). In this way, Na/Li ratios ≤ 5 were always achieved in the Li elution fractions when using 8 mL columns from then on.

Li recoveries after optimization of the separation procedures were typically 99-100 %, as shown in **Table 4**. Complete recovery excludes the possibility of an effect of on-column isotope fractionation on the final data.

In summary, the 8 mL columns are preferred for their higher sample loading capacity and superior elution profiles. Nevertheless, extensive resin precleaning is required to obtain sufficiently low Na/Li ratios. Duration of the isolation procedure, approximately 10 h for a typical set of 8 columns processed in parallel, was similar for all columns, as the larger elution volumes used with the 8 mL columns are compensated for by a higher eluent flow rate. All carbonate samples of an elaborate subsequent study were dissolved in 0.28 M HCl and were loaded onto 8 mL columns to 15 % of their capacity [17].

Evaluation of 2 mL resin columns for Li isolation from digested clay mixtures

From **Figure 3**, it is clear that different elution profiles were obtained for the clay samples, with 100 µl loads resulting in Li elution between 5 and 10 mL, whereas both lower and higher sample load volumes resulted in Li eluting at higher eluent volumes (6,5-14 mL). Tailing of the Li elution peak was observed in three of the elution profiles, which caused an incomplete separation between Li and Na in the respective samples, despite complete Li recovery in all experiments. **Table 5** summarizes the elution volumes containing Li, Li recoveries and Na/Li ratios in the Li elution fractions. It was found that the higher Li elution volumes and peak tailing resulted from columns with a small overload of resin until the bottom of the eluent reservoir on top of the column. Hence, the inferior elution profiles were attributed to a perturbation of the top of the resin during addition of the first eluent portions. In all later experiments, care was taken to lower the resin height to just below the eluent reservoir and to add the first 1 mL of eluent in smaller portions of 100-500 µl. Under the latter conditions, Li eluted in 5 to 10 mL eluent volume. The concentration of the major elements Ca, Mg and Fe was always below the limit of detection in all elution fractions.

Li isotope ratio determination after isolation from carbonate and clay matrices

The column volume was established to have little to no effect on isotope ratio accuracy and reproducibility, as demonstrated via the δ^7Li values obtained for Li IRMM-016 isotopic reference material after chromatographic isolation of Li using the procedures outlined above. Fifteen independent isolations and analyses resulted in an average δ^7Li of 0.1 ‰ and an external precision (2SE) of 0.2 ‰ (N=15). In addition, multiple isolations for sub-samples originating from one carbonate and four clay samples, all resulted in reproducible δ^7Li values. Whether carbonate was dissolved in 0.28 or 0.50 M HCl did not affect δ^7Li values, demonstrating that no Li was leached from the clay into the carbonate fraction during sample preparation. This result is in agreement with the observations made by Von Strandmann et al. [18] An overview of all results obtained upon isotopic analysis of IRMM-016 and of real samples is given in **Table 6**.

Conclusion

When defining a minimum absolute amount of Li of 10 - 20 ng for isotopic analysis via MC-ICP-MS, the analysis of carbonate and clay required an upscaling of existing protocols for analyte isolation because of the high matrix cation load and/or low (≤ 1 µg/g) Li concentrations involved. This technical note presents a method using 2 and 8 mL AG-50W-X8 cation exchange resin loaded into a 25 cm long column, providing quantitative Li recovery from the clay and carbonate fractions of whole-rock carbonate, respectively. In the final, optimized method, 8 mL columns are loaded to 15 % of their capacity with carbonate samples dissolved in 0.28 M HCl, containing < 100 ng of Li, while 2 mL columns are loaded with 100 µl of clay digest (< 1 % of column capacity) containing ~75 ng of Li. Lithium was eluted in the ‘5 to 10’ and ‘15 to 35 mL’ 0.5 M HCl fractions from the 2 and 8 mL columns, respectively. Absence of matrix cations in this fraction was demonstrated. Extensive prewash of the columns with four column volumes of 6 M HCl was important to prevent Na contamination originating from the resin. For both types of samples, this approach permits accurate and precise (external precision (2SE) of 0.2 ‰ (N=15)) Li isotope ratio data to be obtained using MC-ICP-MS. The protocols developed allow Li isotope ratios to be investigated in parallel in these chemically diverse sub-samples (whole-rock carbonate and clay) in a paleoclimatological context. To this end, the protocols were subsequently applied to bulk hemipelagic limestones sampled at high resolution across two Cretaceous-Paleogene (K-Pg) boundary sections (Furlo Pietralata and Fonte d’Olio, Italy). An in-depth interpretation of these results is presented elsewhere [17].

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References

1. Berglund, M., Wieser, M.E., *Pure Appl. Chem.,* 2011, **83**(2), 397–410.

2. You, C.-F., and Chan, L.-H., *Geochimica et Cosmochimica Acta,* 1996, **60**, 909–915.

3. Cameron, A.E., 1955, Variation in the natural abundance of the lithium isotopes: Journal American Chemical Society, v. 77, p. 2731–2733.

4. T. B. Coplen, J. A. Hopple, J. K. Böhlke, H. S. Peiser, S. E. Rieder, H. R. Krouse, K. J. R. Rosman, T. Ding, R. D. Vocke, Jr., K. M. Révész, A. Lamberty, P. Taylor, P. De Bièvre. *Compilation of Minimum and Maximum Isotope Ratios of Selected Elements in*

Naturally Occurring Terrestrial Materials and Reagents. U.S. Geological Survey Water-Resources Investigations Report 01-4222, Reston, Virginia, 2002. http://pubs.usgs.gov/wri/wri014222/pdf/wri01-4222.pdf (last accessed September 2015).

5. J. S. Pistiner, G. M. Henderson, *Earth Planet Sc Lett,* 2003, **214**, 327-339.

6. Y.-J. Tang, H.-F. Zhang, J.-F. Ying, *Int. Geol. Review*, 2007, **49**, 374-388.

7. R. Millot, N. Vigier, J. Gaillardet, *Geochim Cosmochim Ac*, 2010, **74**(14), 3897-3912.

8. L. Chan, J. Edmond, G. Thompson, K. Gillis, *Earth Planet Sc Lett* **108**(1-3), 151-160.

9. J. Wimpenny, S. R. Gíslason, R. H. James, A. Gannoun, P. A.E. Pogge Von Strandmann, K. W. Burton, *Geochim Cosmochim Ac*, 2010, **74**(18), 5259-5279.

10. E. C. Hathorne, R. H. James, Earth Planet Sc Lett, 2006, 246, 393-406.

11. S. Misra, P. N. Froelich, Science, 2012, 335, 818-823.

12. S. Misra, P. N. Froelich, *J Anal Atom Spectrom*, 2009, **24**, 1524-1533.

13. F. W. E. Strelow, *Anal Chem*, 1960, **32**, 9, 1185-1189.

14. T. Magna, U. H. Wiechert, A. N. Halliday*, Int J Mass Spectrom*, 2004, **239**, 67-76.

15. P. B. Tomascak, R. W. Carlson, S. B. Shirey, *Chem Geol,* 1999, **158**, 145-154.

16. T. Moriguti, E. Nakamura, *Chemical Geology*, 1998, **145**, 91–104, 1998.

17. J. Belza, K. Van Hoecke, T. Croymans, S. Goderis, F. Vanhaecke, M. Dumon, E. Van Ranst, S. Misra, A. Montanari, P. Claeys, *under revision*

18. P. A. E. von Strandmann, H. C. Jenkyns, R. G. Woodfine, 2013, *Nature Geoscience*, **6**, 668–672.

Figure captions

Figure 1 – Effect of matrix load (%) and sample volume (mL) on the isolation of Li from whole-rock carbonate using 3 mL resin volume columns.

Figure 2 – Effect of matrix load (%) and sample volume (mL) on the isolation of Li from whole-rock carbonate using 8 mL resin volume columns.

Figure 3 – Effect of sample provenance and load volume on the isolation of Li from digested clay samples using 2 mL resin volume columns.

Table 1

Table 1 - Instrument settings and data acquisition parameters applied for quadrupole-based ICP-MS elemental analysis and MC-ICP-MS isotopic analysis

	XSeriesII	Neptune
Intstrumental settings		
RF power (W)	1200	1120-1320[a]
Cool gas flow rate (L/min)	13.0	15.0
Auxiliary gas flow rate (L/min)	0.74	0.70
Nebulizer gas flow rate (L/min)	0.79-0.84[b]	1.035-1.070[a]
Sampler and skimmer cone	Ni, Xt-type	Ni, H-type
Sample uptake rate (mL/min)	0.5	0.05
Data acquisition parameters		
Resolution setting	n.a.	low
Integration time (s)	0.030	2.1[c]
Blocks	3	5[c]
Cycles/block	100	2[c]
Total data acquisition time	9 s per nuclide	21 s
Total measurement time	9 s per nuclide	41,5 s[d]
Outlier test	n.a.	$\lvert x_i - \bar{x} \rvert > 2\sigma$
Neptune cup configuration		
Cup	Mass/nuclide	Amplifier resistance (Ω)
L4	^{6}Li	10^{12}
C	6,526 amu	10^{11}
H4	^{7}Li	10^{12}

[a]: optimized daily taking into account sensitivity and stability;

[b]: optimized daily taking into account sensitivity, stability and ^{156}CeO^{+}/^{140}Ce^{+} ratio

[c]: minimum measurement time for optimum precision, as indicated by experiments reported in Table 2 and adopted in the final method

[d]:Sum of (i) 10 x 1.05 s baseline cycles, (ii) total acquisition time and (iii) 5 x 2 s idle time at the start of each block

Table 2

Table 2 - Experimental design for optimization of the data acquisition parameters and Li concentration in MC-ICP-MS analysis

Experiment	Integration time (s)	No. of blocks x cycles/block	Data acquisition time (s)	Li concentration (µg/l)	Average δ^7Li (‰)	2SD (‰)	Intensity $^7Li^+$ (V)
1	2.1	15	31,5	10	0.0	0.7	0.3
2	4.2	15	63	10	0.0	0.4	0.3
3	4.2	10	42	25	0.0	0.7	0.8
4	2.1	15	31,5	25	0.0	0.2	0.8
5	2.1	10	21	25	0.0	0.3	0.8
6	2.1	10	21	40	0.0	0.4	1.3
7	4.2	15	63	40	0.0	0.3	1.3
8	2.1	10	21	50	0.0	0.3	1.5

Table 3

Table 3 - Overview of cation exchange chromatographic procedure

Procedure prior to sample loading			
Step	Solution	Volume	
Preload column wash	Milli-Q H_2O	2 column volumes (4, 6 or 16 mL)[a]	
Preload column wash	Ethanol	1 column volume (2, 3 or 8 mL)[a]	
Preload column wash	Milli-Q H_2O	2 column volumes (4, 6 or 16 mL)[a]	
Resin load	AG 50W-X8 in Milli-Q	1 column volume (2, 3 or 8 mL)[a]	
Resin cleaning	6 M HCl	4 column volumes (12, 18 or 48 mL)[a, b]	
Column backwash	Milli-Q H_2O	1 column volume (2, 3 or 8 mL)[a]	
Column conditioning	0.5 M HCl	3 column volumes (6, 9 or 24 mL)[a]	
Sample loading and elution procedure			
Step	2 mL column	3 mL column	8 mL column
Sample loading	65-140 µl clay digest in 0.22 M HCl	1.12 to 3.06 mL carbonate solution in 0.28 or 0.50 M HCl	3.27 to 8.40 mL carbonate solution in 0.28 or 0.50 M HCl
Elution	15 mL 0.50 M HCl	30 mL 0.50 M HCl	60 mL 0.50 M HCl
Li elution fraction[c]	5 to 10 mL	8 to 18 mL	15 to 37.5 mL
Resin cleaning	6 M HCl 2 column volumes (4, 6 or 18 mL)[a]		

[a]: volumes indicated correspond to resin volumes of 2, 3 and 8 mL, respectively.

[b]: Volume resulting from experimental Na and Ca determination in 6 M HCl resin cleaning solution (cf. ESI).

[c]: position of Li elution peak in the optimized methods

Table 4

Table 4 - Experimental design and results for optimization experiments with 3 and 8 mL resin volumes for Li isolation from carbonate matrices

Column capacity	HCl concentration	Ca^{2+} matrix load	Sample load volume (mL)	Li mass load (ng)	Li recovery (%)[a]	Na recovery (%)[a]
3 mL resin volume (5.1 meq)	0.28 M	10 % (10.2 mg Ca)	2.04	26	99	101
	0.28 M	15 % (15.3 mg Ca)	3.06	38	99	85
	0.5 M	10 % (10.2 mg Ca)	1.12	25	100	102
	0.5 M	15 % (15.3 mg Ca)	1.79	38	99	92
	0.5 M	blank	2.00	blank	n.a.	n.a.
8 mL resin volume (13.6 meq)	0.28 M	10 % (28.0 mg Ca)	5.60	70	100	106
	0.28 M	15 % (42.0 mg Ca)	8.40	105	96	101
	0.5 M	10 % (28.0 mg Ca)	3.27	69	100	105
	0.5 M	15 % (42.0 mg Ca)	4.90	104	100	103
	0.5 M	blank	2.00	blank	n.a.	n.a.

[a]: Uncertainty (2*SD) of 3 %

Table 5

Table 5 - Experimental design and results for optimization experiments with 2 mL resin volumes for Li isolation from clays

Clay origin	Sample load (µl)	Li load (ng)	Li elution fraction (mL)	Li recovery[c] (%)	Na/Li
FPL[a]	65	54	6.5 - 11	102	< 1
FPL	100	82	5 - 10	100	< 1
FPL	130	109	6.5 – 13	97	5
FDO[b]	70	53	6.5 - 14	100	23
FDO	100	77	5 - 10	100	<1
FDO	140	106	6.5 - 13	100	9

[a]: Mixture of digested clay samples from Furlo Pietralata locality (Italy)

[b]: Mixture of digested clay samples from Fonte d'Olio locality (Italy)

[c]: Uncertainty (2*SD) of 3 %

Table 6

Table 6 - δ^7Li values obtained after ion exchange chromatographic isolation of Li from isotopic reference material, clay or carbonate samples with MC-ICP-MS.

Column volume	sample	Li concentra-tion	δ^7Li	Column volume	Sample	Li concentra-tion	δ^7Li
mL		µg/L	‰	mL		µg/l	‰
2	IRMM016	50	0.0	2	Clay 1A	50	-1.2
2	IRMM016	50	0.5	2	Clay 1B	50	-1.6
2	IRMM016	50	0.8	2	Clay 2A	50	-2.0
2	IRMM016	50	1.0	2	Clay 2B	50	-1.9
2	IRMM016	50	0.4	2	Clay 3A	50	-1.0
8	IRMM016	25	-0.5	2	Clay 3B	50	-1.0
8	IRMM016	25	-0.3	2	Clay 4A	50	-3.4
8	IRMM016	25	0.0	2	Clay 4B	50	-3.3
8	IRMM016	50	0.1	3	Carbonate 1	25	9.6
8	IRMM016	50	0.1	3	Carbonate 1	25	9.1
8	IRMM016	50	0.3	8	Carbonate 1	25	9.2
8	IRMM016	50	0.1	8	Carbonate 1	25	9.5
8	IRMM016	50	-0.8	8	Carbonate 1	25	9.1
3	IRMM016	50	0.02	8	Carbonate 1	25	9.2
3	IRMM016	50	-0.01				

Figure 1

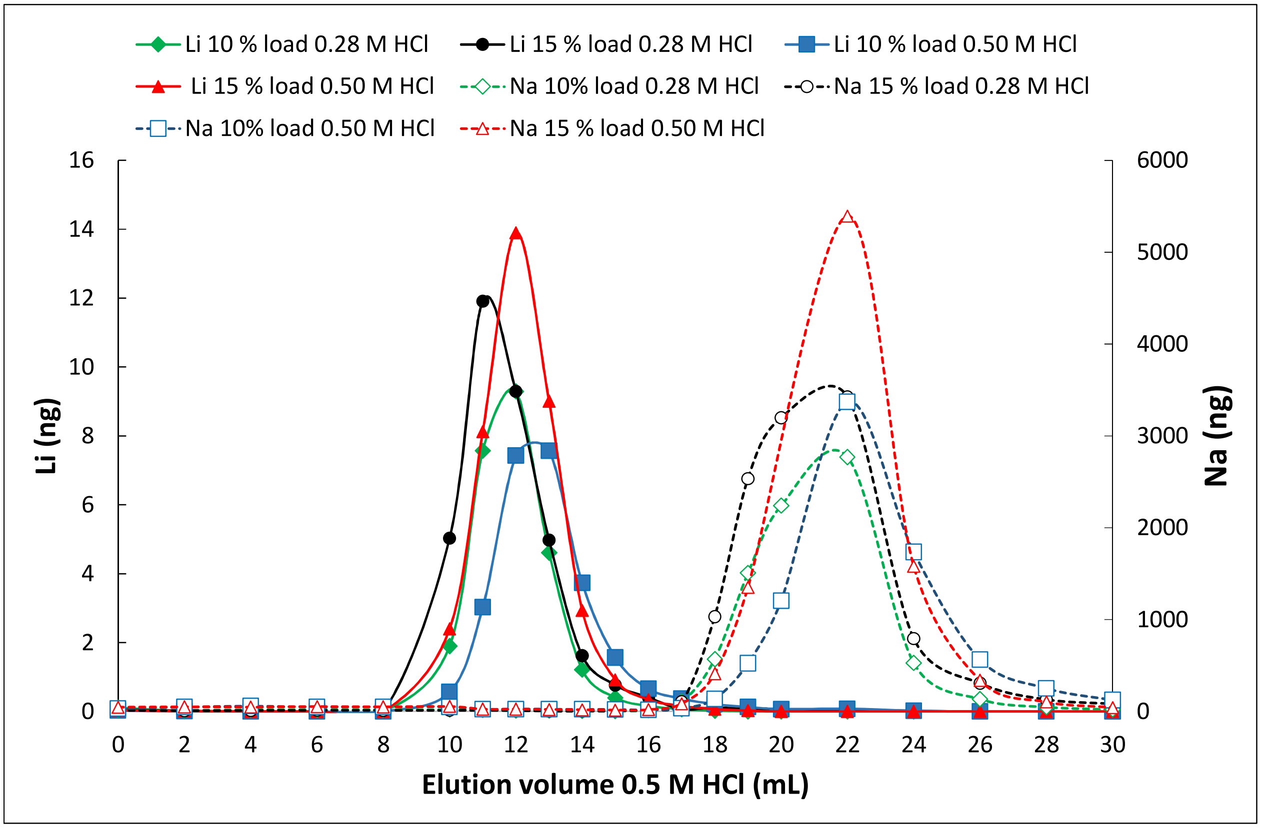

Li 10 % load 0.28 M HCl
Li 15 % load 0.28 M HCl
Li 10 % load 0.50 M HCl
Li 15 % load 0.50 M HCl
Na 10% load 0.28 M HCl
Na 15 % load 0.28 M HCl
Na 10% load 0.50 M HCl
Na 15 % load 0.50 M HCl
Li (ng)
0
2
4
6
8
10
12
14
16
Na (ng)
0
1000
2000
3000
4000
5000
6000
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
Elution volume 0.5 M HCl (mL)

Figure 2

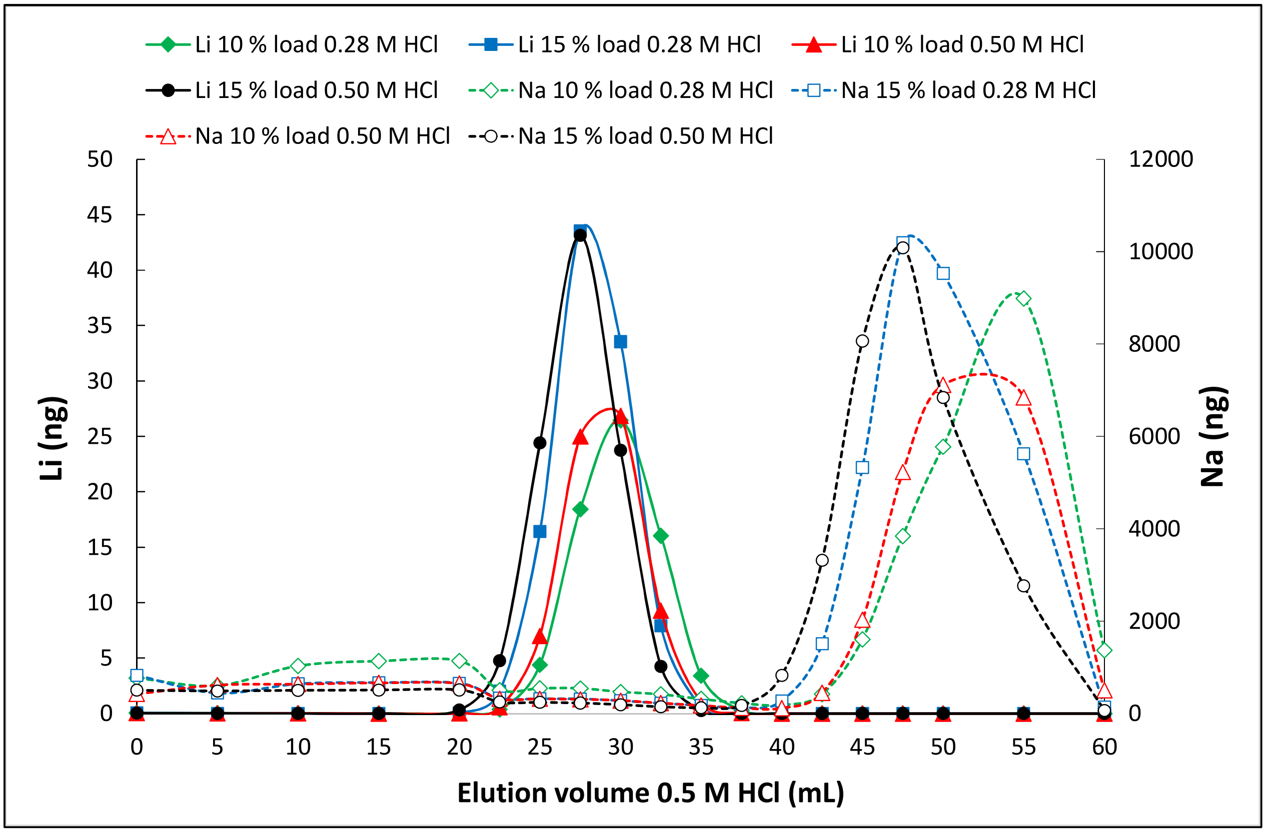
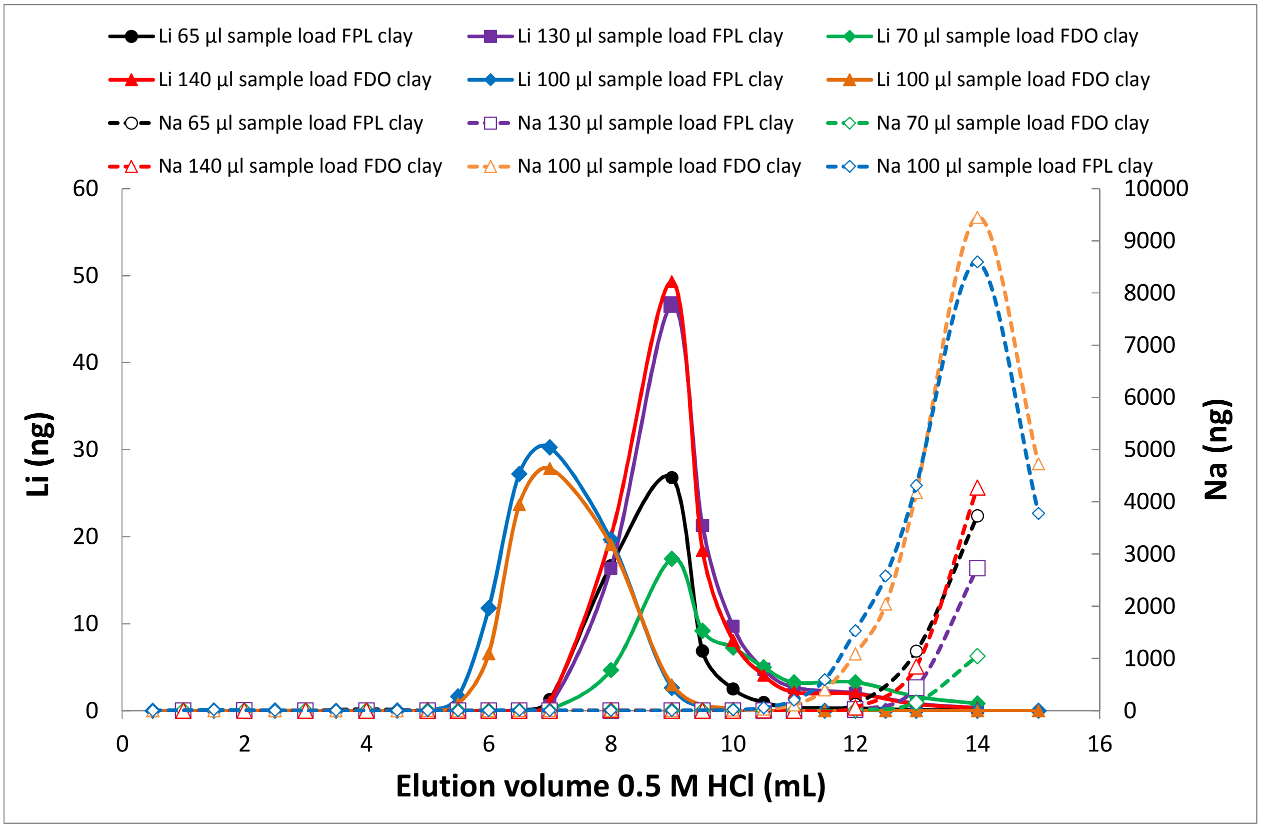

Li 10 % load 0.28 M HCl
Li 15 % load 0.28 M HCl
Li 10 % load 0.50 M HCl
Li 15 % load 0.50 M HCl
Na 10 % load 0.28 M HCl
Na 15 % load 0.28 M HCl
Na 10 % load 0.50 M HCl
Na 15 % load 0.50 M HCl
Li (ng)
0
5
10
15
20
25
30
35
40
45
50
Na (ng)
0
2000
4000
6000
8000
10000
12000
0
5
10
15
20
25
30
35
40
45
50
55
60
Elution volume 0.5 M HCl (mL)

Figure 3


Li 65 µl sample load FPL clay
Li 130 µl sample load FPL clay
Li 70 µl sample load FDO clay
Li 140 µl sample load FDO clay
Li 100 µl sample load FPL clay
Li 100 µl sample load FDO clay
Na 65 µl sample load FPL clay
Na 130 µl sample load FPL clay
Na 70 µl sample load FDO clay
Na 140 µl sample load FDO clay
Na 100 µl sample load FDO clay
Na 100 µl sample load FPL clay
Li (ng)
0
10
20
30
40
50
60
Na (ng)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
0
2
4
6
8
10
12
14
16
Elution volume 0.5 M HCl (mL)