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Development of Li column chemistry procedure for calcium carbonate material

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Table of content

Abbreviations	4
1. Introduction	5
2. Lithium isotope geochemistry	5
2.1. Lithium in Earth's crust	5
2.2. Lithium isotope ratio in geochemistry	6
2.3. Measurement techniques for determination of Li isotope ratios	7
2.3.1. Thermal Ionization Mass Spectrometry - TIMS	7
2.3.2. Quadrupole Inductively Coupled Plasma Mass Spectrometry - Q-ICP-MS	8
2.3.3. Multicollector-Inductively Coupled Plasma Mass Spectrometry - MC-ICP-MS	9
2.3.4. Secondary Ionization Mass Spectrometry - SIMS	10
2.3.5. Lithium column chemistry	11
3. Material and methods	14
3.1. Chemicals and materials	14
3.2. Sample Collection and preparation	15
3.2.1. Sample material	15
3.2.2. Sample Digestion	15
3.2.3. Lithium column chemistry	17
3.3. Measurement procedure	20
3.3.1. ICP-MS Instruments	20
3.3.2. Trace element analysis	20
3.3.3. Calibration standards	21
3.3.4. Quality control standards	22
3.3.5. Isotope ratio measurements	22
4. Results and discussion	22
4.1. Evaluation of HCl molarity	22
4.2. Evaluation of matrix loading	23
4.3. Evaluation of Li loadings	25
4.4. Evaluation of the acid concentration of carbonate dissolution	26
4.5. Results of isotopic ratio measurement	27
5. Conclusion	30

6. Summary	31
7. Kokkuvõte.....	32
8. References	33
9. Appendices.....	37

Abbreviations

TIMS	Thermal Ionization Mass Spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
Q-ICP-MS	Quadruple inductively-coupled-plasma mass spectrometry
MC-ICP-MS	Multi-collector Inductively coupled plasma mass spectrometry
SIMS	Secondary ion mass spectrometry
RF	Radiofrequency
DC	Direct current
ORS	Octopole reaction system
RM	Reference material
PFA	Perfluoroalkoxy alkanes
PP	Polypropylene

1. Introduction

As an element widely distributed in nature, the isotopic composition of Li in sedimentary formations is vital for tracing the past climate events, especially continental weathering, the modern carbon cycle, and the recycling of oceanic crust. In Li isotopic measurement, the signals of the Li isotopes are often interfered with by the matrix components. Hence, ion-exchange column chromatography is necessary to isolate Li from the matrix (particularly Na) during the sample preparation. However, existing ion exchange column methods of separating Li from Na are time-consuming, and single-column elution protocols can cause tailing during the elution procedure, which results in inaccurate isotopic composition measurement due to the incomplete separation or is designed to work under very specific sample loading conditions. The main objective of the current thesis is the development of a relatively fast and robust column to isolate Li from the matrix components in solutions prepared from carbonate material and possibly for calcium phosphate material, which both have a similar bulk cation composition. The column set-up is made by packing 3 mL AG-50W-X8 cation ion exchange resin in a column with a diameter of 7.8 mm. The thesis focuses on the influence of eluent and loading acid concentration, matrix loading and Li content on the performance of the column.

2. Lithium isotope geochemistry

2.1. Lithium in Earth's crust

Lithium, the first element in the alkali group of the periodic table, is presented in the Earth's crust at 20 ppm by kg. In nature, Li is the 33rd most abundant element, found in trace amounts in rocks, soils, surface, ground, and seawater ([Aral et al. 2011](#)).

With the development of society, lithium began to play an increasingly important role in contemporary civilization as a result of societal growth. For example, since the 20th centuries, lithium has become an essential part of battery electrolytes and electrodes due to its high electrode potential. The addition of lithium to the electrolyte battery increases the battery capacity by approximately 20 % and extends its service. Thanks to the discovery of lithium-ion batteries for electronic devices (mobile phone, laptop, electronic vehicle), the field has grown dramatically in the last 20 years. Lithium and lithium salts are also widely used in the production of ceramics and glass products as lithium can help enhance the glass properties, including chemical resistance, transparency to ultraviolet or infrared radiation, and photosensitivity. Furthermore, the introduction of lithium compounds is a common silicon

flux treatment that lowers the melting point and viscosity of the molten material, improving the physical properties of glaze coatings and thermal expansion coefficients (Kudryavtsev 2016). In terms of human wellbeing, lithium could primarily be used to treat bio-disorder, such as manic depression.

Furthermore, lithium has been proven helpful in the treatment of major depression, particularly when used in the augmentation of antidepressants (Crossley et al. 2007). Lithium can contribute to air purification. Because lithium chloride and lithium bromide are hygroscopic, they are usually used as desiccants for gas streams. Besides, lithium is essential in nuclear energy, metallurgy, air purification, military, chemical synthesis, and other industries. Although the lithium market used to be small, the demand-driven by modern technology is increasing and requires many sources. Therefore, lithium scientific research has a promising future.

2.2. Lithium isotope ratio in geochemistry

There are two natural isotopes of lithium, ${}^6\text{Li}$ and ${}^7\text{Li}$, in nature. The average terrestrial relative abundance of ${}^6\text{Li}$ and ${}^7\text{Li}$ is around 7.6% and 92.4%, respectively (Berglund et al. 2011). Similar to other stable isotope systems, Li isotopes ratio $\delta^7\text{Li}$ is reported as per mil deviations from the NIST-8454 L-SVEC standard and represented in a delta notation: (Aral et al. 2011)

$$\delta^7\text{Li} (\text{‰}) = \left[\frac{({}^7\text{Li}/{}^6\text{Li})_{\text{sample}}}{({}^7\text{Li}/{}^6\text{Li})_{\text{L-SVEC}}} - 1 \right] \times 1000 \quad (1.)$$

In nature, the fractionation of the two isotopes is very common. Their composition in a mineral depends on the exchange mechanism with the given environment (fluids, melts and adjacent minerals). Based on the LiCO_3 isotope reference material L-SVEC ($\delta^7\text{Li}$ of 0.0‰), the value of $\delta^7\text{Li}$ is varied in different samples. For example, the value of $\delta^7\text{Li}$ in seawater is around +31‰ (Millot et al. 2004), but the variation of $\delta^7\text{Li}$ value in freshwater samples (river water, lake water, groundwater, and spring) ranges from +3 to +36‰ (Meier et al. 2017). The isotopic composition of calcitic sedimentary carbonates that do not contain aragonite is $\delta^7\text{Li} = 6.1 \pm 1.3\text{‰}$ (2σ), but the value of pure aragonite carbonates is $9.6 \pm 0.6\text{‰}$ (2σ) (Pogge von Strandmann et al. 2019b). The change of the value of $\delta^7\text{Li}$ illustrates the mechanism of the Li isotope fractionation. During the period of primary clay mineral dissolution and secondary clay mineral formation, the lighter isotope ${}^6\text{Li}$ is preferentially retained in the solid phase,

while the heavier isotope ^7Li is released into the liquid phase and gradually enriched (Pistiner et al. 2003). Hence, the Li isotopic determination can be used to analyze the interaction between water and rock, which aids in the study of continental weathering and the modern carbon cycle.

Due to the considerable changes in the isotopic composition in nature during the period of continent weathering, quantifying the extent of isotope fractionation is vital in examining the weathering process in both modern and past environments. Several fields of research have achieved this. For instance, (Wimpenny et al. 2010) investigated lithium isotopic ratios to examine the effects of dissolution of primary phases and the formation of secondary minerals during basalt weathering. (Dellinger et al. 2015) reported how the weathering regimes affect the Li isotope fractionation in the Amazon River basin. The experimental work by (Wimpenny et al. 2015) studied the effect of critical physical and chemical parameters on lithium isotopic fractionation—temperature, pH, reacting mineral.

The values of $\delta^7\text{Li}$ on the Earth's surface have also been related to the behavior of some elements that are critical to the carbon cycle, such as Ca, Mg and Fe. The transport of Ca and Mg to form carbonate in the ocean is driven by the chemical weathering process, and marine calcium carbonate precipitation is a crucial sink in the carbon dioxide atmosphere. (Pogge von Strandmann et al. 2019a) studied the relationship between the relative mobility of Li compared to Ca. Revealing that the behavior of Li isotopes in water can be used to quantitatively trace the mobility of Ca (or other elements critical to the carbon cycle).

Furthermore, the isotopic ratio also provides the possibility to study the past climate change because marine carbonates can directly incorporate Li into the CaCO_3 lattice. As a result, determining the Li isotopic ratio in carbonate fractions isolated from whole-rock limestones allows for an investigation of the behavior of continental weathering as a climate proxy.

2.3. Measurement techniques for determination of Li isotope ratios

In order to determine the Li isotopic ratios, several techniques are currently available. Even though these instrumentations and their technical aspects are extraordinarily complicated and expensive, the data outputs are highly accurate and precise.

2.3.1. Thermal Ionization Mass Spectrometry - TIMS

Before the diversification of ICP and SIMS instruments, thermal ionization was the primary method for producing high-precision Li isotopic compositions for several decades. The first

absolute Li isotopic compositions were determined in stone meteorites by TIMS (Balsiger et al. 1968). It is still the only method to measure the absolute Li isotope abundance directly because plasma-based and SIMS instruments always generate mass biased results, and instrument fractionation is too large and variable to effectively correct to absolute ratio. As such, TIMS has represented a cornerstone for resolving even slight differences in $\delta^7\text{Li}$, considering ± 1 ‰ errors that are routinely obtained (Chan 1987).

Furthermore, TIMS has undergone much development at the end of the 20th century. There are several types of research developed to be employed in polyaromatic species. For example, the determination of $^6\text{Li}/^7\text{Li}$ ratios using Li_2BO_2^+ ions analyzed by TIMS with ion counting has been studied by numerical simulation and experiment (Bickle et al. 2000). The study by (Green et al. 1988) showed the development of a Li isotope analysis method based on measurement of Li_2F^+ ion by TIMS. Concerning the metal Li^+ , (Ahmed et al. 2002) developed a method to achieve the stable emission of Li^+ ion with a single SiO_2^- coated Re filament configurations.

However, TIMS gradually became outdated after the invention of MC-ICP-MS. It is more time-consuming and provides lesser opportunity to monitor shifts in instrumental mass bias. Although TIMS has many drawbacks, it is still the sole technique to determine the absolute Li isotope composition, which is critical for scientists to validate Li isotope reference materials.

2.3.2. Quadrupole Inductively Coupled Plasma Mass Spectrometry - Q-ICP-MS

Q-ICP-MS is a mass spectrometry that ionizes a sample using inductively coupled plasma and has a quadrupole mass filter. After ionization, it produces atomic and small polyatomic ions that can be detected. Four conductive and parallel rods, which are mostly made of gold-coated ceramic or molybdenum, make up a quadrupole. An electrostatic field is generated in the space between the opposing rods by applying radiofrequency (RF) and direct current (DC) potentials to each pair of opposing rods, which can filter out non-analyte, and interference. As a result, only the analyte ions with a certain mass-to-charge ratio (m/z) reach the detector that is an electron multiplier where all m/z ratios are collected sequentially in short intervals. Although the plasma-based technique was invented in the early 1980s, the method was not applied widely to Li isotope composition's determination. The earlier generation of single-collector quadrupole ICP instruments was not suitable for isotopic determinations in geological materials as they could not achieve a precision better than 1% (Grégoire et al. 1996; Vanhoe et al. 1991). Despite the more considerable uncertainty of Li isotopic

measurements by this technique, it was applied to lithium's isotopic analysis in human blood and urine (Sun et al. 1987).

Some scientists have improved the quadrupole ICP-MS method for the determination of Li isotopic analysis in geological samples. For example, (Košler et al. 2001) separated Li quantitatively before the measurement on ICP-MS to avoid the matrix-induced isotopic fractionation, so this method was successfully used to measure Li isotopic composition of 1-10 mg geological sample with reproducibility approaching $\pm 2\%$ (2σ). The study by (Misra et al. 2009) demonstrated a new chromatographic method that quantitatively recovers and separates lithium from the matrix and optimized the procedure for analyzing natural carbonates. In recent years, (Liu et al. 2019a) developed a new protocol with less sample consumption and better long-term precision of 1.1% (2σ) to determine the Li isotopic ratio, using Q-ICP-MS operated under hot plasma conditions (1550 W).

Nevertheless, compared with the diversity of MC-ICP-MS, the Q-ICP-MS is a less-used alternative approach for Li isotopic determination. However, for studies for which precision of $\pm 1.0\%$ is suitable, it is still a viable method for measurement. Additionally, the Q-ICP-MS technique shows higher matrix tolerance ($\text{Na/Li} < 100$), suitable for trace analysis and high-matrix geological samples (Liu et al. 2019a). The ICP source also allows flexibility in how samples are introduced to the mass spectrometer, allowing for analysis of samples introduced as an aspirated solution or aerosol produced by laser ablation.

2.3.3. Multicollector-Inductively Coupled Plasma Mass Spectrometry - MC-ICP-MS

Multicollector-Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) is an instrument that is used to measure isotopic composition in geochemistry, geochronology, and cosmochemistry. MC-ICP-MS is a hybrid mass spectrometer that measures ions using an inductively coupled plasma source, an energy filter, a magnetic sector analyzer, and multiple individual detectors. After introducing the sample into the plasma source, which strips off electrons to create positively charged ratios. These ions are accelerated (up to 10 kV) and directed using a series of slits and electrostatically charged plates. The ion beam is then passed through an energy filter (Electrostatic Analyzer), resulting in a consistent energy range in the ion beam, and then passes through a magnetic field, where the ions are divided by the m/z ratio. These mass-resolved beams entered Faraday cup detectors where the ions are converted into voltage. By comparing voltages from different collectors, the isotopic composition can be determined. For low abundance isotopes, electron multiplier detectors are

used to measure the signals. The main advantage of MC-ICP-MS systems over more conventional Q-ICP-MS is the ability to measure multiple m/z signals simultaneously. This feature greatly reduces the variation of the signal ratios that arise from the instability of the plasma and sample introduction, producing a signal drift.

Concerning the determination of Li isotope composition, MC-ICP-MS appears less susceptible to undesired shifts in measured $^7\text{Li}/^6\text{Li}$ ratios than TIMS, resulting from the presence of matrix elements due to imperfect chemical separation of Li (Jeffcoate et al. 2004; Magna et al. 2004; Nishio et al. 2002). However, compared with Q-ICP-MS, MC-ICP-MS is more susceptible to matrix composition. Although the fractionation rate of the Li isotopic ratio with MC-ICP-MS is stronger than TIMS, measuring samples bracketed by standard parentheses effectively solves this problem.

When (Tomascak et al. 1999b) found that the precision of the first-generation of MC-ICP-MS is conservatively estimated to be $\pm 1.1\%$ (2σ), which is similar to the precision of TIMS. In recent years, the study (Magna et al. 2004) achieved significantly better precision and reproducibility (around 0.4% 2σ) using more modern instruments.

At present, some studies are developing the technique. For example, (Le Roux 2010) presented the first laser ablation MC-ICP-MS technique for the measurement of Li isotopes. In the study, it appeared that the combination of LA with MC-ICP-MS might result in the rapid determination of Li isotopic compositions on the sub-0.1 mm scale if followed by technical improvements in detection limits and sensitivity.

2.3.4. Secondary Ionization Mass Spectrometry - SIMS

SIMS is an ionization technique that revolutionized the analysis of a wide variety of polar and biological molecules in the mid-twentieth century and is still commonly used in isotopic ratio determination. SIMS uses a continuously focused primary ion beam to remove material from the sample surface by sputtering. The fraction of the ionized sputtering material is extracted into a double-focusing mass spectrometer, which uses electrostatic and magnetic fields to separate ions based on their m/z ratio. Although MC-ICP-MS represents a new, direct, accurate, and exact detection method for Li isotopic composition determination, secondary ion mass spectrometry (SIMS) technology is far ahead in spatial resolution, sensitivity, and overall technical capability to study Li isotopic composition.

Dynamic SIMS is used to assess the elemental composition and amounts of trace impurities and dopants in solid materials with a depth resolution of better than 10 nm. It is highly sensitive, capable of detecting fractions in the range of parts per million to parts per billion. The first actual attempts to determine the composition of Li isotopes with a secondary or sputtering ion source were performed on meteorites (Poschenrieder et al. 1965; Gradsztajn et al. 1967) and lunar rocks (Eugster et al. 1971).

The matrix-induced fractionation of Li isotopes may create additional uncertainty in measurements. Many researchers have studied the matrix impact on measurement results over the last two decades. (Marks et al. 2008) did a detailed study about SIMS–MC-ICP-MS cross-calibration of pegmatitic Na-rich arfvedsonite and aegirine to determine the matrix effects caused by SIMS. For NIST 610, 612, and 614 glasses, these authors found a significant difference in $\delta^7\text{Li}$ between MC-ICP-MS and SIMS at the level of 4–5 ‰, which indicates the presence of a considerable matrix effect in SIMS determination of Li isotopes. (Kasemann et al. 2005) found a significant matrix bias in high-silica material and the discrepancies in the order of approximately 10‰. The research by (Bell et al. 2009) found that the effect is a linear function of composition for magnesian olivine, with $\delta^7\text{Li}$ increasing by 1.3‰ for each mole percent decrease in the forsterite component. At higher Fe content, the relationship ceases to be linear (Bell et al. 2009).

In conclusion, for elemental detection limits ranging from parts per million to parts per billion, SIMS is the most sensitive surface analysis technique. Due to the significant variation in ionization probabilities among elements sputtered from different materials, comparison against well-calibrated standards is needed to obtain accurate quantitative results.

2.3.5. Lithium column chemistry

At present, scientists have developed accurate and precise methods for Li isotopic analysis. However, the measurements are susceptible to interferences, and matrix effects cause significant instrument mass-dependent isotopic fractionation due to the ionization of the non-analytes. Besides, M/Li ratios in natural samples usually exceed 10^4 (e.g., Na/Li in seawater), and the similarity of the ion exchange portioning of Li to some major cations makes isolating Li from the matrix difficult.

For Li separation, cation ion exchange resin is widely used. The chemical groups bonded to the beads in a cation exchange column are negatively charged. Positively charged molecules in a mixture passing through the column will exchange with the counter-ions and attach to the

negatively charged groups on the beads, while the neutral or negatively charged compounds will flow rapidly through the column (Ahern et al. 2019). The separation is based on the physical properties and chemical composition of both the ion exchanger and the ion, so it can be applied to lithium separation. Dowex 50W X2 cation exchange resin with 150 -200 μm diameter was used to successfully separate Li (Mikeš et al. 2017). And AG50W X8, 200- 400 mesh, also shows great separation ability (Li et al. 2019). Besides the resin, the volume of the resin also affects the Li separation. For example, (Van Hoecke et al. 2015) compared 3mL and 8 mL resin column for Li isolation from carbonate sample and showed that the complete separation was achieved when using 8 mL column, while the 3 mL column shows a slight overlap between Li and Na elution peaks. The research by (Li et al. 2019) demonstrates that a 2 mL resin column does not have the ability to completely isolate Li from matrix, while using a single long column (9 cm) with a smaller diameter can achieve complete separation.

In previous researches, it is proven that some mineral acids such as HCl and HNO₃ can effectively be used to separate Li and other elements by ion-exchange chromatography (Strelow et al. 1974). The study shows that using 0.5 M HCl as eluent can narrow the Li elution ranges, leading to faster elution. The mixture of mineral acid and organic solvent can increase the elution fraction peak resolution and improve the separation, resulting in more effective removal of most cations and high field-strength elements (Korkisch et al. 1967; Huang et al. 2010). Some research shows that using 1.5 M HNO₃ + 70% methanol mixture has some disadvantages. For example, rapid volatilization of methanol changes the eluent composition during the leaching (Ai et al. 2014). Besides, the evaporation of methanol can decrease the air solubility and produce air bubbles in the resin (Jeffcoate et al. 2004), which can cause significant shifts in the elution peaks of Li and Na. Moreover, organic matters in the final elution fraction can interfere with the isotopic measurement (Chernonozhkin et al. 2015).

To achieve good Li/matrix separation, relatively large resin loadings, high aspect ratio, and large eluent volumes are required, so the efficiency of a column system must be considered. Early attempts at isolating Li from volcanic materials necessitated the use of three or four different columns (Moriguti et al. 1998; James et al. 2000; Rudnick et al. 2004). These procedures are time-consuming and necessitate a significant amount of eluent, which both increase the possibility of contamination. After that, scientists started to use a single column to separate Li from the other matrix components. Some studies (Lin et al. 2016; Tomascak et al. 1999a; Van Hoecke et al. 2015) show that the whole separation process of a single column

system takes approximately 7-10 hours. In addition, incomplete Li separation leads to on-column fractionation (Misra et al. 2009).

Optimization of the separation and improvement of the efficiency can be achieved by changing the column separation conditions, such as eluent, matrix loading, resin volume, and the number of columns. The details about chemical separation procedures and experimental designs for various column systems are given (Table 1). However, a single-column approach may not be sufficient, so the separation protocol needs to be calibrated separately for completing the removal of matrix elements and full recovery of Li during chromatography (Tomascak et al. 2016; Van Hoecke et al. 2015; Phan et al. 2015).

Table 1. chemical separation procedures for various column systems

Column	Single-column A (Phan et al. 2015)	Single-column B (Van Hoecke et al. 2015)	Single-column C (Van Hoecke et al. 2015)	Single-column D (Li et al. 2019)	Dual-column (Li et al. 2019)
Parameters	A short column with 2 mL resin (height:4 cm)	A short column with 2 mL resin (height:4 cm)	A short column with 2 mL resin (height:4 cm)	A long column with 2.5 mL resin (height: 9 cm)	1st long column with 2.5 mL resin (height: 9 cm) 2nd short column with 2 mL resin (height: 4 cm)
Sample loading	1 mL sample (10-20 mg) digest in 1.5 M HNO ₃ + 70% methanol	1 mL sample (10–20 mg) digest in 0.2 M HCl	1 mL sample (10–20 mg) digest in 0.5 M HCl	2 mL sample (10–20 mg) digest in 0.2 M HCl	1st long column 2 mL sample (10–20 mg) digest in 0.2 M HCl 2nd long column dried collection digest in 0.2 M HCl
Collection	21 mL 1.5 M HNO ₃ + 70% methanol	30 mL 0.2 M HCl	30 mL 0.5 M HCl	60 mL 0.2 M HCl	1st long column (0.2 M HCl; 18–44 mL collected) 2nd short column (0.2 M HCl, 1–3 mL; 0.5 M HCl, 4–16 mL; 7–16 mL collected)

Table 1 (continued).

Column	Single-column A (Phan et al. 2015)	Single-column B (Van Hoecke et al. 2015)	Single-column C (Van Hoecke et al. 2015)	Single-column D (Li et al. 2019)	Dual-column (Li et al. 2019)
Post column check	2 mL 1.5 M HNO ₃ + 70% methanol	2 mL 0.2 M HCl	2 mL 0.5 M HCl	2 mL 0.2 M HCl	1st long column 2 mL 0.2 M HCl 2nd short column 2 mL 0.5 M HCl
Resin cleaning	20 mL 6.5 M HCl 15 mL ultra-pure water	20 mL 6 M HCl 15 mL ultra-pure water	20 mL 6 M HCl 15 mL ultra-pure water	40 mL 6 M HCl 15 mL ultra-pure water	1st long column: 40 mL 6 M HCl + 15 mL ultra-pure water 2nd short column: 20 mL 6 M HCl + 15 mL ultra-pure water

3. Material and methods

3.1. Chemicals and materials

All solvents and chemicals used in the study were of supra pure or higher grade. Ultra-pure water (18.2 MΩ cm) was produced using a Milli-Q water purification system. H₂O₂ (Sigma Aldrich, Ultrapure) was used to clean the natural samples (Coral and Clam samples) from organic residues. Solutions made from 69% HNO₃ (Carl Roth, ROTIPURAN Supra), 35% HCl (Carl Roth, ROTIPURAN Supra), and 48% HF (Carl Roth, ROTIPURAN Supra), were used for cleaning vials and containers. Material dissolution and storage of sample solutions was performed in 10 mL PP (Polypropylene) tubes that were soaked in 2% HNO₃ for 24h, rinsed with Milli-Q water 3 times, soaked in 2% HNO₃ and 1% HF mixture at 40°C for 24h, rinsed 3 times with Milli-Q and airdried in a fume hood. 5mL PP sample tubes that were used to collect samples from elution profiling experiments were soaked in 2% HNO₃ for 24h, rinsed with Milli-Q water 3 times, and airdried in a fume hood. 20 mL PFA vessels that were used to collect eluate for isotope ratio measurements were cleaned using 20mL Aqua Regia (3:1 HCl: HNO₃) on a hotplate at 80°C for 24h rinsed 3 times with Milli-Q and airdried in a fume hood. 35% hydrochloric acid (Carl Roth, ROTIPURAN Supra) was diluted to the required molarities as necessary with Milli-Q water for column cleaning and elution. Multi-

element 10 ug/mL calibration standard solution 2A was obtained from Agilent Technologies (CA, USA), which was used for evaluation of the isolation procedure and for calibration of elemental concentration analysis. For isotope ratio analysis, LSVEC Li₂CO₃ reference material stock solution was prepared by dissolving 11 mg in 100 mL of 0.5 M HCl.

3.2. Sample Collection and preparation

3.2.1. Sample material

For optimization of the isolation of lithium from calcium carbonate matrix, 200 mL of stock solution was prepared by dissolving 4 g of natural limestone from Rägavere formation, Estonia. The dissolution was performed in 0.5 M HCl for 1 h and the solid residue (14 wt%) was discarded. The concentration of Li and Na in the stock solution were 8.65 and 1820 µg/L, respectively. Other carbonate materials and certificated reference materials with different lithium isotope ratios were used to evaluate the effectiveness of the developed column procedure via measurement of respective lithium isotope ratios. The geological samples and reference materials that were used in this study are as follows:

Natural limestone from Rägavere formation, Estonia (Carbonate stock), was obtained from a drill core material. TR-18-26 and TR-17-5 were carbonate samples from the Tartu drill core number 8. The coral sample was provided by the University of Tartu Estonian Marine Institute, collected from the northern Atlantic, and was divided into two parts according to the different visual characteristics. The white external part is located in the inner surface of the coral (C-EX), while the grey internal part is between the white part and the outermost surface (C-IN); Clam sample was provided by the University of Tartu Estonian Marine Institute from the Norwegian coast (Clam); Apatite NP (apatite powder, Li 1.1 µg/g) was provided by myStandards GmbH; BCR-2 (basalt powder, Li 9.13 µg/g) reference material by USGS. BCR-2 is not a carbonate material, but its $\delta^7\text{Li}$ is well characterized, and the preferred mean value is 3.04 (0.53 SE) ‰ LSVEC.

3.2.2. Sample Digestion

Sample solutions were prepared at the sediment laboratory at the University of Tartu. Samples were dissolved in 0.5 M HCl solution while different sample preparation procedures were used due to limitations in sample size and sample matrix.

Carbonate sample from Rägavere (Carbonate stock), clam, and apatite sample was crushed to powder, then 4g Carbonate, 0.2002g Clam, 0.1018g Apatite powder were digested with 200 mL, 10 mL, and 10 mL 0.5 M HCl solution, respectively until total dissolution was achieved.

10-fold dilution carbonate stock solution was prepared for low loading test by adding 9 mL 0.5 M HCl and 1 mL carbonate stock solution. These sample solutions were preserved in 500 mL (Carbonate) or 10 mL acid-washed PP tubes (clam, apatite, 10-fold diluted carbonate stock solution).

2 more 5 mL carbonate solutions were prepared as 2x and 3x Li carbonate stock solutions, which were used for evaluating the effect of different content of Li on the separation between Li and Na. The carbonate stock solution was spiked with 4.32 and 8.64 μ L multi-element calibration standard solution 2A, respectively, to achieve desired Li concentration.

In addition, 5 mL carbonate stock solution were transferred into 2 PFA vessels and heated on a hotplate to complete dryness. Then these carbonate sample residues were redissolved in 0.05 and 0.1 M HCl, respectively, which were used to evaluate how the acid concentration affects the Li separation.

With regards to the coral sample, sample material was homogenized in an agate mortar, and 0.3874g Coral- EX and 0.0055g Coral-IN powder were weighed into two PFA vials. 4 mL and 2mL H₂O₂ respectively were added for removal of organic residues. After placing the samples on a hotplate (50°C) for 30 min, solutions were transferred to PP tubes and centrifuged for 10 min at 5000 rpm. After discarding the supernatant, the residues were washed with Milli-Q water and centrifuged again. Finally, the residues were dissolved in 20 and 2 mL 0.5 M HCL, respectively.

Sample solutions of TR-18-26 and TR-18-5 samples were prepared by dissolving 150 mg of sample material in 7 mL of 0.5M HCl for 1 h. The samples were then centrifuged for 10 min at 5000 rpm, and the supernatant was collected and stored for column chemistry in 10mL PP tubes.

BCR-2 was dissolved using 4 concentrated acid digestion on the hotplate. 0.2 g of BCR-2 was weighed into a PFA vessel. 3 mL HCl, 2 mL HNO₃, 1 mL HClO₄, and 2.5 mL HF were slowly added in turn. The PFA vessel was placed on the hotplate (80°C) for 1 h and after that heated at 110°C to incipient dryness. The temperature was then raised to 160°C, and the sample was heated to complete dryness. After removing PFA vessels from the hotplate and letting it cool, 1 mL of concentrated HClO₄ was slowly added and again evaporated (160°C) to complete dryness. When the sample residues cool to room temperature, they were

redissolved in 10 mL 0.5 M HCl solution. The prepared BCR-2 was kept in a 10 mL acid-washed PP tube.

3.2.3. Lithium column chemistry

For the single column tested in this study, separation of Li from other matrix components was performed using Dowex 50W-X8 (Acros Organics, Belgium) cation exchange resin (200 – 400 mesh) with a Cation binding capacity of 1.7 Meq/mL. 3 mL wet resin bed volumes (in Milli-Q water) were packed into an empty PP column with an internal diameter of 7.8 mm, corresponding to a resin height of 6.3 cm. Prior to usage, the resin-packed columns must be cleaned to remove any residual cations from the column. Hence, the column after resin loading was washed sequentially with 3 mL 6 M HCl 4 times and 3 mL Milli-Q water, then rinsed 3 times with 3 mL 0.5 M HCl to condition the column. A general protocol for the preparation of columns for Li isolation via cation chromatography, as well as a description of the column washing procedures and the detail of the columns, are shown in [Table 2](#). Once elution was finished, the ion exchange column needs to be regenerated by repeating the cleaning, washing, and conditioning steps. All cleaning operations were performed in fume hoods following all general precautions to reduce contamination.

Table 2. Overview of preparing cation exchange chromatography

Step	Solution	Volume (mL)
Resin loading	Dowex 50W-X8 in Milli-Q	3 (1 column volume)
Column cleaning	6 M HCl	12 (4 column volumes)
Column wash	Milli-Q H ₂ O	3 (1 column volume)
Column conditioning	0.5 M HCl	9 (3 column volumes)

Optimization of the method for the isolation of Li from carbonate matrices was carried out using carbonate stock solution, which was made from the limestone sample from Rägavere (Carbonate stock). In order to optimize the elution solution (HCl) concentration, the HCl molarity test was performed to find the most suitable concentration to isolate Li.

Subsequently, different matrix loadings, Li loading and acid concentration in sample solution were used to study the shifts of the Li elution range. All matrix loadings were calculated based on the dissolved carbonate sample mass, assuming CaCO₃ composition for unknown

carbonate samples. For BCR-2 and Apatite NP, calculations for loading were based on reference composition data.

In the HCl molarity test, after loading 1.27 mL carbonate stock sample solution (8.6% Ca²⁺ matrix loading according to the column capacity), the column was eluted with 10x 3 mL of different molarity HCl (0.15 M, 0.2 M, 0.25 M, 0.3 M, 0.35 M, 0.4 M, 0.45 M, 0.5 M). 5 mL PP tubes were used to collect individual 3 mL elution fractions.

Due to the difficulty in sampling for some geological samples and only a small amount of sample can be obtained, and the matrix of the samples can be diverse as such evaluation of different matrix loading was performed. Carbonate stock solutions with different matrix loading (1% - 30% of the total resin capacity) were loaded onto the ion exchange column and eluted with a total of 30 mL 0.3 M HCl solution. Individual 1 - 3 mL elution fractions were collected in respective 5 mL PP tubes. The detail of experiment design is presented in [Table 3](#).

In both experiments, individual elution fractions were collected in 5 mL pp tubes and diluted 10 times before measurement. The concentrations of Li and Na in all fractions were determined by quadrupole ICP-MS.

Table 3. Experiment design of matrix loading test with 3 mL resin volumes for Li isolation from carbonate matrices. Column separation was achieved using 0.3 M HCl as eluent, which was the optimized HCl concentration.

Matrix loading (%)	Sample solution	Sample loading volume (mL)	HCl (M)
1	10x diluted carbonated stock solution	1.47	0.3
2	10x diluted carbonated stock solution	2.94	0.3
10	Carbonate stock solution	1.47	0.3
15	Carbonate stock solution	2.21	0.3
20	Carbonate stock solution	2.94	0.3
25	Carbonate stock solution	3.68	0.3
30	Carbonate stock solution	4.41	0.3

Because the exact composition of the natural sample is unknown, the different content of Li may affect the separation between the Li and Na. To evaluate the effect of Li concentration on the elution of Li from the columns, a multi-element calibration standard (Agilent 2A) was used to spike the stock carbonate solution to increase the concentration 2 and 3-fold, relative to the stock carbonate solution. The carbonate stock solution with 1 x, 2x, and 3x Li were respectively added onto the column at 10% and 20% column loading and eluted with 30 mL 0.3 M HCl solution. Individual 1 ~ 3 mL elution fractions were collected in different 5 mL PP tubes. The information about the experiment design is presented in [Table 4](#).

Table 4. Experiment design of Li loading test with 3 mL resin volumes at the same matrix loading level for Li isolation from carbonate matrices. Column separation was achieved using 0.3 M HCl, which was the optimized HCl concentration.

Sample	Spiked Li (ng)	Matrix load	Sample loading volume (mL)	HCl (M)
Carbonate stock solution	0	10%	1.47	0.3
Carbonate stock solution with 2x Li	12.7	10%	1.47	0.3
Carbonate stock solution with 3x Li	25.4	10%	1.47	0.3
Carbonate stock solution with 2x Li	12.7	20%	2.94	0.3
Carbonate stock solution with 3x Li	25.4	20%	2.94	0.3

To explore the influence of acid concentration of carbonate dissolution on the performance of the column. 1.47 mL (10% matrix loading) of the above-prepared sample solutions dissolved in 0.05 and 0.1 M HCl were loaded onto the column and eluted with a total of 30 mL 0.3M HCl solution. In all the above experiments, individual elution fractions were collected in 5 mL pp tubes and diluted 10 times before measurement. The concentrations of Li and Na in all fractions were determined by quadrupole ICP-MS.

After evaluating the separation between the Li and Na by using carbonate stock solutions, carbonate samples, natural samples, and reference materials were used to validate the effectiveness of the columns. Thus, sample solutions with different loading were loaded on the column and eluted with 0.3 M HCl. Li elution fractions were collected in PFA vessels, which were placed on the hot plate (50°C) and evaporated to dryness. Then the residues were redissolved in 0.22 M HCl. In addition to the Li elution fractions, pre- and post-cuts, corresponding to 3 mL of eluates before and after the Li elution fraction were collected to validate that the whole Li elution peak was collected in the Li elution fraction. The collected Li elution fraction was used for the determination of the Li recovery and the corresponding isotopic ratio. The isotopic ratio was expressed using the delta notation, whereby $\delta^7\text{Li}$ is calculated according to equation (1) and expressed in ‰ deviation from LSVEC standard values.

3.3. Measurement procedure

3.3.1. ICP-MS Instruments

Agilent Technologies 8800 Triple Quadrupole ICP-MS in the Department of Geology at the University of Tartu was used to determine the elemental concentrations and Li isotopic composition. The ICP-QQQ 8800 is a tandem ICP-MS with two hyperbolic quadrupoles separated by an octopole reaction system (ORS). As a result, ion-gas reactions can be performed in the ORS. The first quadrupole selects the precursor ions that access the ORS cell, pressurized with either an inert collision gas (He) or a reactive gas (H₂, O₂, NH₄). The ion will undergo charge transfer or coupling reactions that produce new molecular ions with a higher m/z ratio. The second quadrupole is then used to select the product ions formed in the cell, then reach the electron multiplier detector.

Two different instrument parameters were used in the study, respectively, for trace element content and the isotopic ratio determinations.

Instrumental parameters of the ICP-MS system are given in [Table 5](#).

3.3.2. Trace element analysis

For concentration analysis, the following isotopes were measured in No-Gas mode: ⁷Li, ²³Na, ²⁴Mg, ²⁷Al, ³⁹K, ⁴³Ca, ⁴⁴Ca, ⁵⁷Fe. Measurement conditions are described in [Table 5](#).

¹¹⁵In was used as an internal standard and added via mixing-T.

Table 5. Instrumental operating and data acquisition parameters

	Element analysis	Lithium isotopic measurement
Instrumental settings		
RF power (W)	1100	800
RF matching (V)	1.7	1.5
Sampling depth (mm)	7	5.5
Nebulizer gas flow rate (L/min)	0.9	0.75
Data acquisition parameter		
Resolution setting	Standard	Standard
Integration time (s)	⁷ Li – 1 ²³ Na, ²⁴ Mg, ²⁷ Al, ³⁹ K, ⁴³ Ca, ⁴⁴ Ca, ⁵⁷ Fe, ¹¹⁵ In – 0.5	⁶ Li, ⁷ Li – 30
Number of sweeps	30	1000
Total acquisition time (s)	16.261	322
Number of replicates	3	5
Sample uptake time (s)	50	60
Stabilize time (s)	40	90
Probe sample rinse time (s)	80	120
Probe standard rinse time (s)	80	120

3.3.3. Calibration standards

The calibration standard was Agilent Technologies multi-element calibration standard 2A. The calibration solutions were prepared in the range of 0.01 to 100 µg/l. (0.01, 0.05, 0.1, 0.5, 1, 5, 10, 50, 100 ppb). Every 10-15 samples, a secondary calibration standard with a concentration of 1 or 2.5 µg/l was measured and used to calculate a secondary correction factor for the measured data.

3.3.4. Quality control standards

The NIST 1643f (Trace elements in water) quality control standard was analyzed at a 10-fold dilution of the original standard. This solution was analyzed alongside secondary calibration standards to ensure that the measurement procedure was accurate.

3.3.5. Isotope ratio measurements

Measurements of lithium isotope ratio were performed in a standard-sample-standard bracketing configuration. The sensitivity of the instrument was around 500000 cps/1ppb. All samples were diluted to a final concentration of 2 $\mu\text{g/l}$ for measurement, and each sample measurement was bracketed by measurements of L-SVEC standard of the same concentration as the sample. If the initial sample contained less than 2 $\mu\text{g/l}$ Li, the bracketing standards were diluted to match the concentration of the sample. Each sample signal was corrected for mass bias based on the signal of the bracketing L-SVEC standards. Instrument configuration is presented in [Table 5](#).

4. Results and discussion

4.1. Evaluation of HCl molarity

The elution profiles of the 3 mL column eluted with different eluent (HCl) concentrations are shown in Fig. 1. With increasing HCl concentration, the peak of Li and Na are both shifted towards the smaller volume and gradually approach each other and start to overlap. Higher concentration HCl has higher extraction ability than lower concentration HCl, resulting in faster elution and a narrower elution range of Li fraction. Although 0.15 - 0.25 M HCl can separate the Li from the Na, it takes a long time, and more eluents are needed to collect the Li elution fraction. When the column is eluted with 0.4 to 0.5 M HCl, the chromatograms showed a slight overlap between Li and Na elution peaks, and it becomes more severe with the increase of HCl concentration. These results illustrate that the single short column with 3 mL resin cannot completely separate Li from Na when eluent with HCl molarities over 0.35M. Therefore, 0.3 M was chosen as the optimized concentration, where the Li can be efficiently separated from Na. In the following experiments, 0.3 M HCl was always used as the eluent, and the whole elution procedure took around 4 hours. The concentration of other matrix elements (K, Ca, Mg, Al, Fe, and Sr) should be eluted after Na.

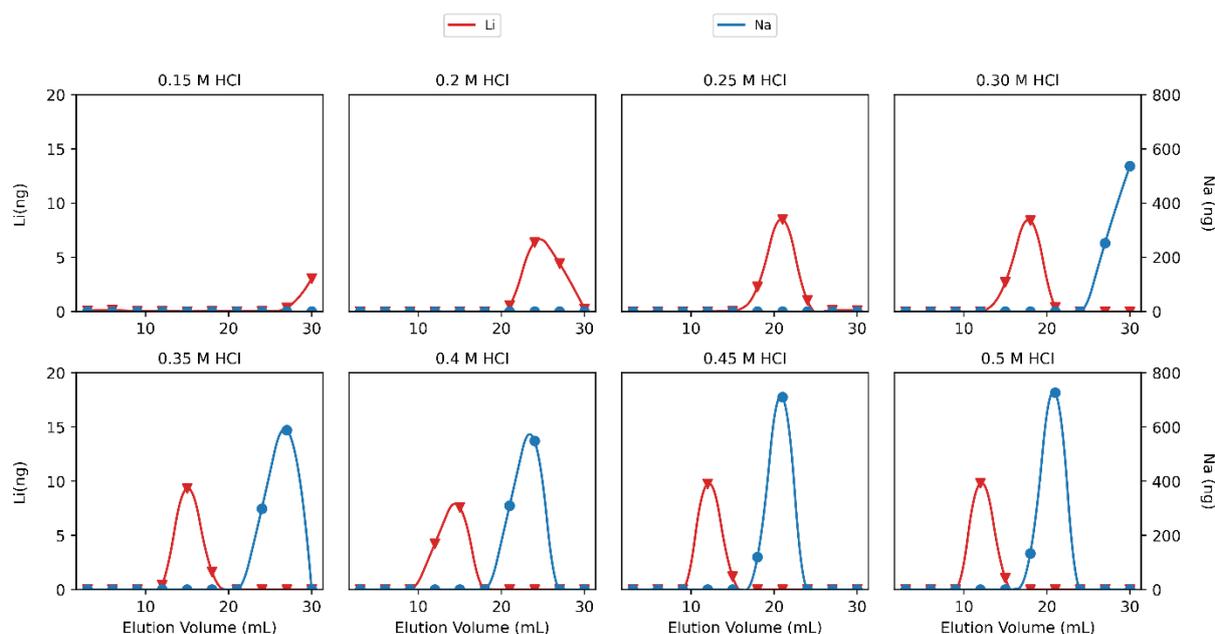


Fig. 1 effect of eluent concentration (HCl molarity) on the isolation of Li from carbonate matrix using 3 mL resin volume column

4.2. Evaluation of matrix loading

Fig. 2 shows the elution profiles of the 3 mL rinse column from the five Ca^{2+} matrix loading experiments listed in Table 3. As we can see, the elution range separating Li from Na shifts towards smaller volume as the Ca^{2+} matrix loading increases from 10% to 30%. For example, at 10% matrix loading, the Li starts to elute in the range from 12 mL to 17 mL and decreases to 0 at 20 mL, while the Na eluting starts at 24 mL. Similarly, the elution volume range for 20% matrix loading is 10 mL to 18 mL, and there is no minor tailing of Li's elution peak before Na's. It can be observed that with increasing matrix loading, the elution of Li and Na shifts to lower elution volumes and move closer together with Li and Na starting to overlap at 30% matrix loading. Therefore, the 3 mL resin column can achieve complete isolation of Li from Na under high matrix loadings above 25%.

Fig. 3 compares the effect of low Ca^{2+} matrix loading using the repeated regenerated 3 mL resin column and fresh-made new 3 mL resin column. From the profile of the old column, we find the Li contamination existed in the elution fractions as the existence of Li is detected in the whole elution volume range where Li should not be present. There is no Li contamination when the column was first used for molarity tests and 10% ~ 30% Ca^{2+} matrix loading tests according to previous results. However, minor Li appears before the Li elution peak after several times of regeneration, followed by a large amount of Li contamination in the

subsequent low Ca^{2+} matrix loading tests. This phenomenon is known as Li bleeding, which may happen during the elution after the columns were regenerated and reused several times. The mechanism of the Li bleeding is unclear, but a simple solution is to make a new column packed with new resin for each elution.

Regarding the performance of low matrix loading in the fresh column, the elution peaks shift slightly to higher elution volumes and are narrower (15-21 mL) compared with the profile of 10% loading (12-20 mL). The elution of Na started from approximately 25 mL in both 1% and 2% loading. Furthermore, there is no Li bleeding when using a fresh column, which means Li can be completely isolated from the Na in this case.

To sum up, the 3 mL resin column shows excellent ability to separate Li from the carbonate matrix from 1% to 25% matrix loading. Still, different matrix loading will cause a shift in the elution range, and the collected elution volume range must be adjusted accordingly. Li bleeding may happen if the columns are reused. In order to avoid this, fresh columns should be prepared for each experiment.

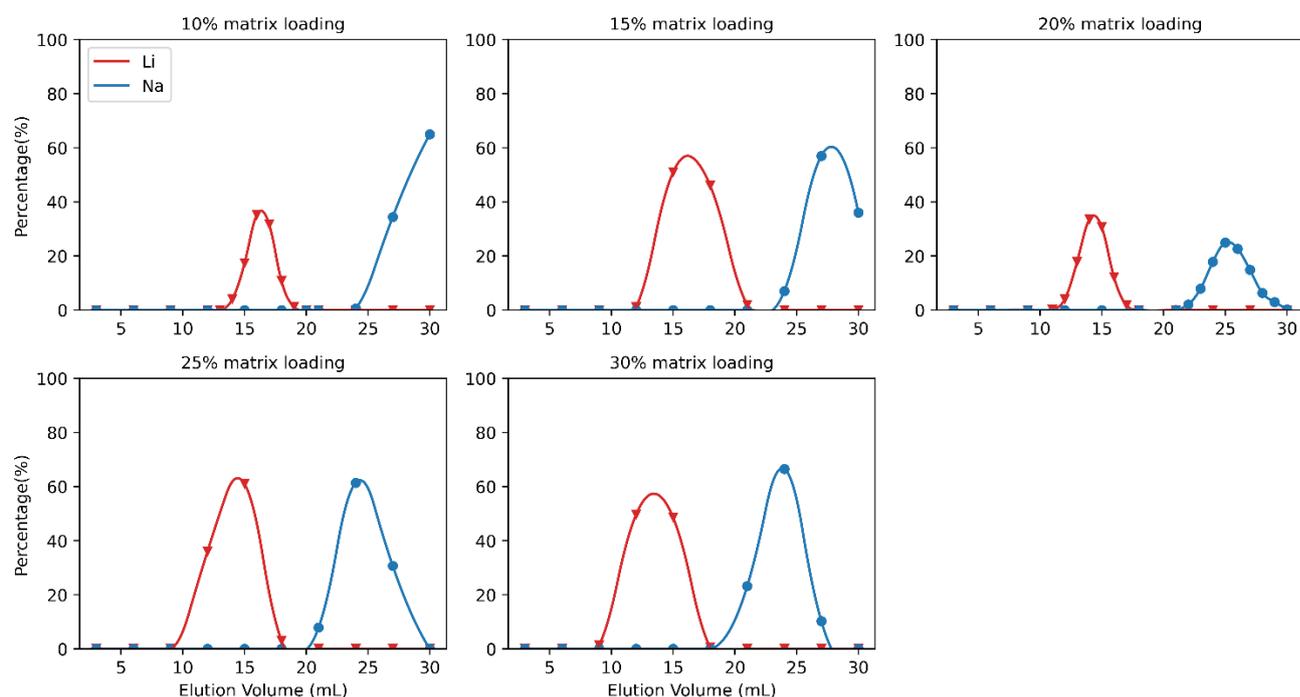


Fig. 2 Effect of Ca^{2+} matrix loading (10% to 30% of total resin capacity) on the isolation of Li from carbonate matrix using 3 mL resin volume column

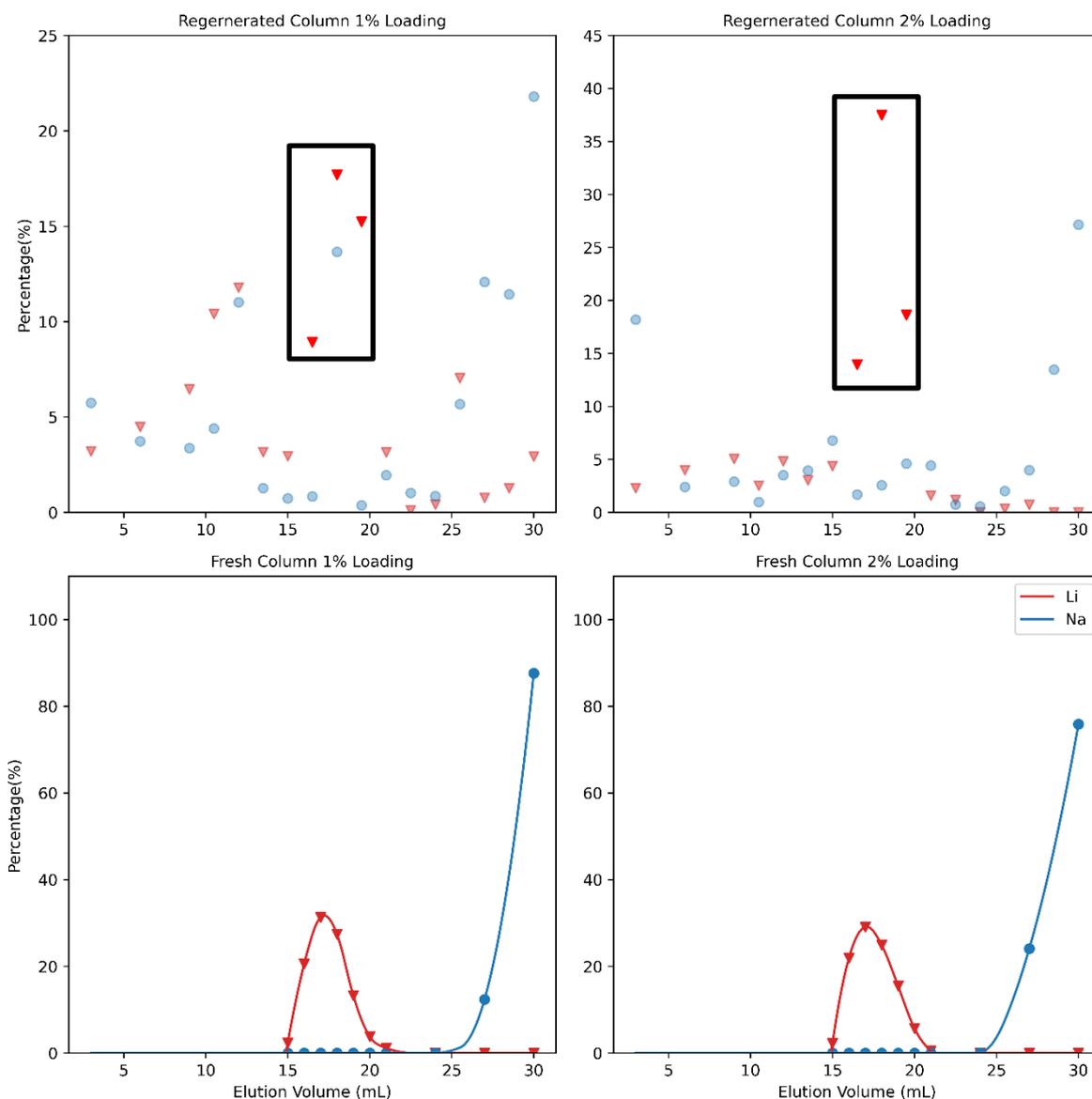


Fig. 3 Comparison of the effect of low Ca^{2+} matrix loading (1% and 2% of total resin capacity) on the isolation of Li from carbonate matrix using 3 mL resin regeneration column and fresh column

4.3. Evaluation of Li loadings

As most natural samples and reference materials have a relatively low content of Li, it is necessary to evaluate the effect of the amount of loaded Li on the elution of Li. Fig. 4 shows the elution profiles of the 3 mL rinse column from all experiments with double and triple Li listed in Table 4. It is evident that increasing the Li amount to double or triple loading does not have influence the elution range. As for all 10% matrix loading, the Li elution fraction range is approximately from 12 mL to 20 mL. With regard to 20% matrix loading, the Li

elution fraction range is around 10 to 18 mL. The elution fraction ranges are both the same as the results in the loading test showed in Fig.3.

In conclusion, the experiment confirmed that the Li loadings do not affect the Li separation, but the matrix loading causes a shift of the Li elution profile peak.

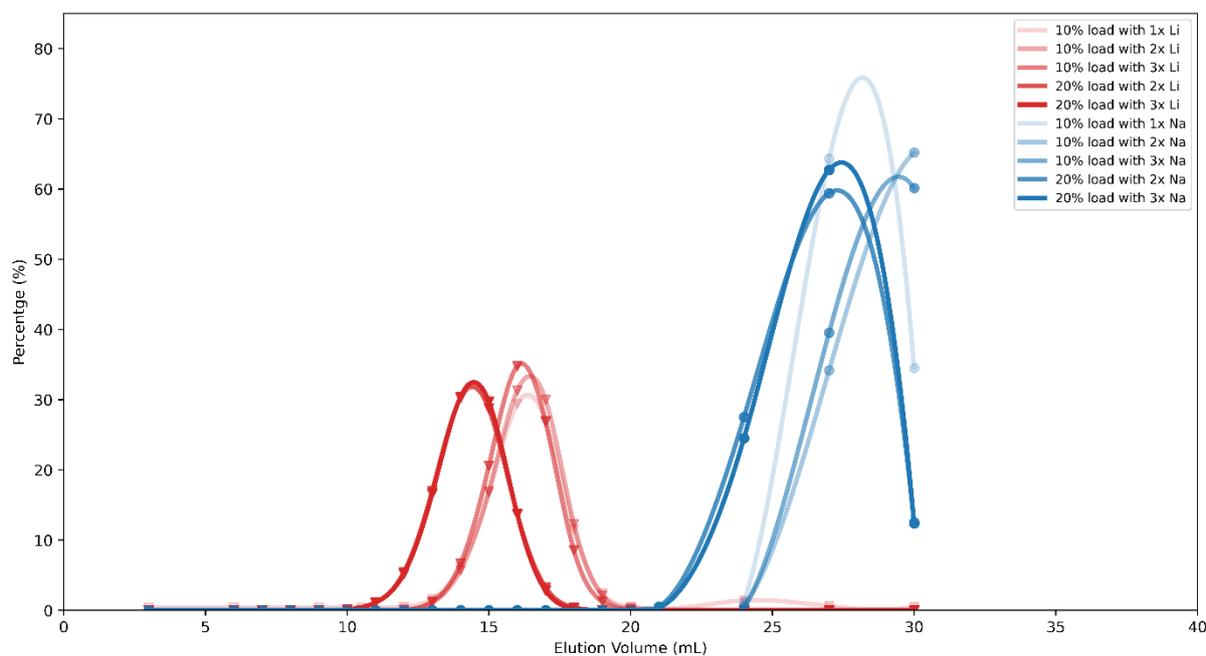


Fig. 4 Effect of Li loadings with 10% and 20% matrix loading (% of total resin capacity) on the isolation of Li from carbonate matrix using 3 mL resin volume column

4.4. Evaluation of the acid concentration of carbonate dissolution

Fig.5 illustrates how the HCl concentration of sample solution affects the Li separation when using 10% matrix loading. The Li elution volume ranges from the sample solution digested in 0.05 M and 0.1 M HCl are 13-20 and 13-19 mL, and the elution maxima shifts from 17mL to 16mL, respectively. This shift could be caused by slight variations in the physical properties of the column as the elution range overlaps with 0.5 M HCl loading. Na starts to elute from 24 mL. The separation between Li and Na is the same as the results of the sample digested in 0.5 M HCl with 10% Ca²⁺ matrix loading (shown in Fig.4 and Fig.3). Therefore, the HCl concentration of acid used for digestion will not greatly influence the Li isolation.

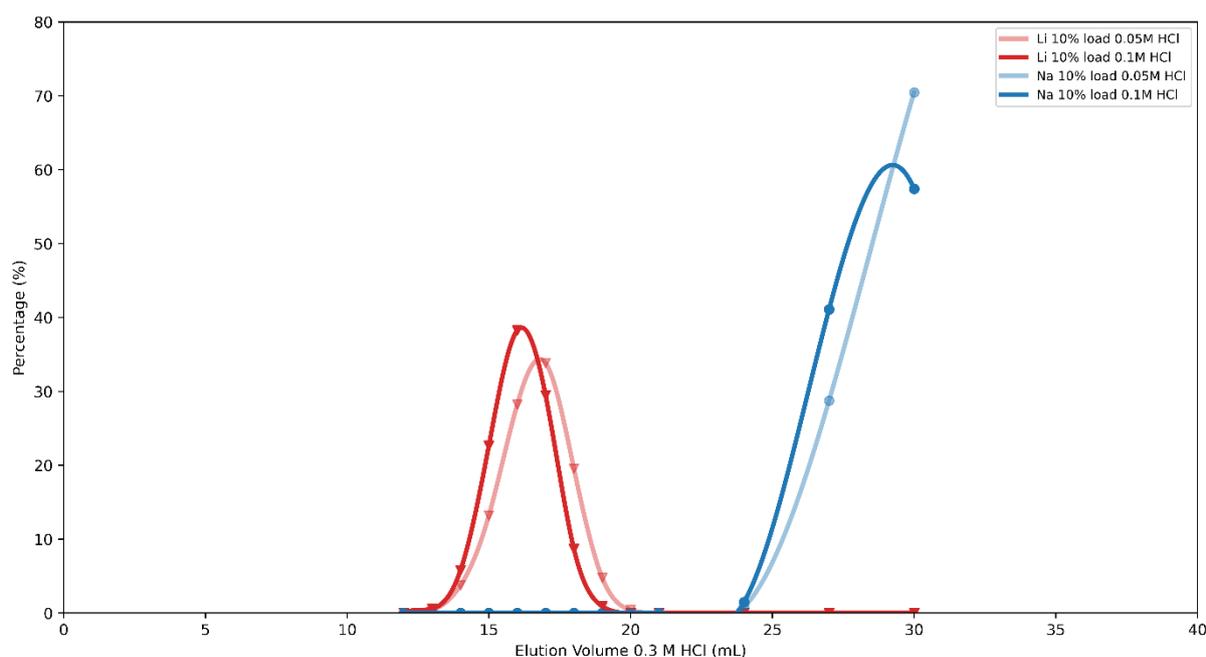


Fig. 5 Effect of low acid concentration of loaded sample solution (0.05 M and 0.1 M HCl) with 10% matrix loading on the isolation of Li from carbonate matrix using 3 mL resin volume column

4.5. Results of isotopic ratio measurement

The $\delta^7\text{Li}$ values obtained from BCR-2 reference material and other natural samples are shown in Table 6. All the sample solutions were measured after the 3 mL resin column separation using the procedures presented in the methodology. The obtained values are used to validate the entire procedure. The measurement uncertainty of the reference materials and geological samples is two standard deviations of the individual measurement consisting of 5 replicas.

The values of $\delta^7\text{Li}$ of most of the samples analyzed in the study are within the range of the values reported in the literature or obtained from comparative measurements. The value of $\delta^7\text{Li}$ of BCR-2 measurement is $3.40 \pm 1.01\text{‰}$, which is constituent with the 3 latest reference values reported in 2019 as $3.02 \pm 0.51\text{‰}$ (2σ) (Li et al. 2019), $3.16 \pm 1.1\text{‰}$ (2σ) (Liu et al. 2019b) and $3.19 \pm 0.39\text{‰}$ (2σ) (Zhu et al. 2019) and the mean value ($3.04 \pm 0.53\text{‰}$). The results from 2% loading of TR-18-5 ($11.41 \pm 0.88\text{‰}$) and 26 ($11.16 \pm 0.41\text{‰}$) are essentially identical to the average values of those samples that were determined with 10% loading and by a separate column set-up in development ($11.45 \pm 0.87\text{‰}$ and $11.38 \pm 0.88\text{‰}$). Apatite is a reference material under development, and its reference value of $\delta^7\text{Li}$ is unknown so far. So the measured value of $\delta^7\text{Li}$ serves as an initial reference value ($1.80 \pm 0.94\text{‰}$).

The value of the coral external part ($17.18 \pm 1.05\text{‰}$) coincides directly with the reported average value for the most recent crystallized part of aragonitic corals grown in seawater $\delta^7\text{Li} = 17.3 \pm 0.7\text{‰}$ (Bastian et al. 2018). As the sample mass for the coral's internal part was small and contained a low amount of lithium, the Li concentration of the solution after the column chemistry is only 0.36 mg/L of Li. The analysis of this sample was bracketed by L-SVEC standards that were diluted to the same concentration level. Due to the lower signal intensity, the measured isotopic ratio was less precise and gave a value of $13.4 \pm 2.1\text{‰}$. Inhomogeneity of $\delta^7\text{Li}$ in coral has been hinted at by (Bastian et al. 2018), who reported a large variation in a homogenized coral reference material JCp1. This fractionation could be due to vital effects in the coral and need further analysis for confirmation. The $\delta^7\text{Li} = 16.9 \pm 1.7\text{‰}$ from the Clam sample corresponds to the range of aragonitic clam values reported by (Dellinger et al. 2018), ranging from +16 to +22‰, with lower values corresponding to clams growing in colder waters.

Table 6: Comparison of $\delta^7\text{Li}$ measured value of geological samples and isotopic reference materials using 3 mL resin column and reference value.

Sample/RM	Type	Matrix loading (%)	Sample loading volume (mL)	Li elution fraction range(mL)	Li content (ug/L)	Measured $\delta^7\text{Li}$ (‰)	Measured uncertainty (‰)	Reference value (‰)	Uncertainty (‰)
BCR 2	Basalt	1%	1.28	15 - 22	0.83	3.40	1.01	3.04	0.53
Apatite NP	Apatite Powder	10%	2.62	12 - 22	4.06	1.81	0.94	-	-
Coral-EX	Coral	10%	1.52	15 - 22	2.81	17.18	1.05	17.3	0.7
Coral-IN	Coral	1.6%	1.70	15 - 22	0.36	13.44	2.11	17.3	0.7
Clam	Clam	10%	1.47	12 - 22	2.27	16.94	1.69	16-22	-
TR-18-5	Carbonate	2%	1.47	15 - 22	2.20	11.41	0.88	11.45	0.87
TR-18-5	Carbonate	10%	1.47	12 - 22	20.73	10.05	1.20	11.45	0.87
TR-18-26	Carbonate	2%	1.47	15 - 22	3.34	11.16	0.41	11.39	1.09
TR-18-26	Carbonate	10%	1.47	12 - 22	16.15	12.11	0.79	11.39	1.09

5. Conclusion

A relatively fast and robust ion exchange column was developed for isolating Li from other matrix components in carbonate samples for Li isotope ratio measurements. A 7.8 mm diameter column was packed 3 mL AX-50W-X8 cation exchange resin. The elution procedure takes around 4 hours, which significantly shortens the elution time compared with the existed methods. Effects of 4 parameters on the efficiency of Li isolation: acid concentration of eluent and sample solution, matrix loading, and Li loading were investigated, and it can be concluded that: (a) higher concentration of the eluent (HCl) shifts Li elution to lower elution volume, but the concentrations above 0.35 M lead to incomplete separation of Li and Na, with 0.3 M as optimized molarity. (b) Higher matrix loading shifts elution range to lower volumes. (c) Li concentration and HCl concentration of the sample solution will not affect the Li elution range. (d) After several regenerations of the resin, Li bleeding may happen during the elution procedure, and fresh resin should be used during each experiment. The $\delta^7\text{Li}$ values from the reference material and natural samples agree well with the published literature data. The BCR-2, coral external part, and clam are consistent with the reference value from literature. The $\delta^7\text{Li}$ values of TR-18-26 and TR-18-5 are also according to the average value from the comparative measurement. Therefore, the column shows great performance on efficiency and robustness.

6. Summary

Development of Li column chemistry procedure for calcium carbonate material

The element, Li has two isotopes in nature, ${}^6\text{Li}$ and ${}^7\text{Li}$, with an average terrestrial relative abundance of 7.6% and 92.4%, respectively. The composition of the two isotopes in minerals is varied with the formation process of different samples. This is because, during the primary clay mineral dissolution and secondary mineral formation, the ${}^6\text{Li}$ will retain in the solid phase, but the ${}^7\text{Li}$ prefer the liquid phase. The Li isotope ratio is usually expressed as $\delta^7\text{Li}$, which can be used as a proxy to explore the behavior of continental weathering, the oceanic crust, and the drawing down of CO_2 from the atmosphere. However, the isotopic measurement is easily interfered with by the instrument mass-dependent fractionation caused by non-analyte ionization.

The current thesis is aimed to develop a relatively fast and robust column for complete isolation of Li from calcium carbonate and possibly for calcium phosphate material that has similar bulk cation composition. The study evaluates the effect of the molarity of eluent, matrix loading, Li and the acid concentration in the sample solution. A number of reference materials and geological samples (BCR-2, Apatite NP, coral, clam, TR-18-5, and TR-18-26) are used to validate the isotopic measurement results.

Comparison of results from the same amount of carbonate solution eluted with different HCl concentrations revealed that 0.3 M HCl is the optimal concentration of eluent. The matrix loading tests are based on loading carbonate samples with 1% to 30% matrix loading and are eluted with 0.3 M HCl, which shows the elution range of Li and Na both shift to the smaller volume with increasing loading. The Li and digested acid concentration in the loaded sample solution do not affect the separation between Li and Na.

It is noticed that the Li bleeding gradually happened after the column is several regenerated and repeated use. The mechanism of the phenomenon is not clear, but the solution to avoid the Li bleeding is always use a fresh column for column chemistry.

The isotopic measurement is achieved by Q-ICP-MS, and all samples' solutions are eluted with 0.3 M HCl using the 3 mL resin column. Most of the $\delta^7\text{Li}$ values from the measurement show great agreement with the $\delta^7\text{Li}$ from published literature and comparative results.

7. Kokkuvõte

Li kolonnkeemilise protseduuri välja töötamine kaltsiumkarbonaatsele materjalide analüüsiks

Li eksisteerib looduses kahe stabiilse isotoobina, ${}^6\text{Li}$ ja ${}^7\text{Li}$, mille suhteline sisaldus on vastavalt vastavalt 7,6% ja 92,4%. Kahe isotoopi koostis mineraalides varieerub erinevate proovide moodustumisprotsessist. Selle põhjuseks on asjaolu, et esmase savimineraali lahustumise ja sekundaarse mineraali moodustumise käigus seotakse ${}^6\text{Li}$ eelistatult tahkesse faasi, kuid ${}^7\text{Li}$ eelistab vedelat faasi. Li-isotoopide suhet väljendatakse tavaliselt $\delta^7\text{Li}$ kujul, mida saab kasutada hindamaks kontinentaalse murenemise ulatust, ookeanilise maakoorekoore käitumise ja atmosfäärse CO_2 sisalduse muutusi. Li isotoopsuhete mõõtmist raskendab mitte-analüüdi ionisatsiooni poolt indutseeritud instrumendipõhine fraktsioneerumine.

Käesoleva töö eesmärgiks on välja töötada suhteliselt kiire ja robustne kolonn Li täielikuks eraldamiseks kaltsiumkarbonaatsetest ja võib-olla kaltsiumfosfaatsetest materjalidest, millel on sarnane katioonkoostis. Töös hinnatakse kuidas mõjutavad eluendi molaarsus, kolonni koormamine ning Li ja happe kontsentratsiooni proovilahuses kolonni efektiivsust. Isotopsuhete mõõtmistulemuste valideerimiseks kasutati erinevaid võrdlusmaterjale ja geoloogilisi proove (BCR-2, Apatite NP, korallid, karp, TR-18-5 ja TR-18-26).

Erinevate HCl kontsentratsioonidega elueeritud sama koguse karbonaadilahuse tulemuste võrdlus annab tulemuseks, et 0,3 M HCl on optimaalne eluendi kontsentratsioon. Kolonni koormamiskatsed põhinesid karbonaatproovide lisamisel 1 - 30% kolonni sidumisvõimakusest ja elueeritakse 0,3 M HCl-ga, mis näitasid, et nii Li kui ka Na elueerimisvahemik nihkuvad suuremal koormamisel väiksemate eluaarimisvahemike suunas. Li ja happe kontsentratsioon proovilahuses ei mõjuta Li ja Na eraldumist.

Kui kolonni on mitu korda regenereeritud ja korduvalt kasutatud, tähendati Li vabanemist kogu elueerimisvahemikus. Nähtuse mehhanism pole selge, kuid Li püsiva vabanemise vältimiseks tuleks kolonnkeemia reakendamisel alati kasutada värsket katioonvahetit.

Isotopsuhete mõõtmine teostati Q-ICP-MS abil ja kõigi proovide lahused elueeriti 0,3 M HCl-ga, kasutades 3 mL kolonni. Suurem osa mõõtmise $\delta^7\text{Li}$ väärtustest langevad hästi kokku varasemalt avaldatud tulemuste ja võrdlusanalüüside tulemustega.

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9. Appendices

Appendix No.1 The Li content of elution fraction in HCl molarity test

Comparing the Li content in every elution fraction to see how the concentration of HCl (0.15 – 0.5 M) affects separation between the Li and Na.

Molarity (M)	Elution fraction (mL)	Li (ng)	Na (ng)	Li (%)	Na (%)
0.15	3	0.08	0	2.25	0
	6	0.13	0	3.49	0
	9	0.04	0	1.04	0
	12	0.04	0	1.00	0
	15	0.00	0	0.12	0
	18	0.04	0	0.95	0
	21	0.01	0	0.23	0
	24	0.03	0	0.81	0
	27	0.35	0	9.36	0
	30	3.05	0	80.75	0
0.20	3	0	0	0	0
	6	0	0	0	0
	9	0	0	0	0
	12	0	0	0	0
	15	0	0	0	0
	18	0	0	0	0
	21	0.57	0	4.93	0
	24	6.37	0	54.77	0
	27	4.44	0	38.16	0
	30	0.25	0	2.14	0
0.25	3	0	0	0	0
	6	0	0	0	0
	9	0	0	0	0
	12	0	0	0	0
	15	0.04	0	0.30	0
	18	2.28	0	18.92	0
	21	8.48	0	70.35	0
	24	1.03	0	8.58	0
	27	0.12	0	0.97	0
	30	0.10	0	0.87	0
0.30	3	0	0	0	0
	6	0	0	0	0
	9	0	0	0	0
	12	0	0	0	0
	15	2.70	0	23.51	0
	18	8.40	0	73.15	0
	21	0.38	0	3.34	0
	24	0	0	0	0
	27	0	252	0	31.99

The table continued

Molarity (M)	Elution fraction (mL)	Li (ng)	Na (ng)	Li (%)	Na (%)
	30	0	536.37	0	68.01
0.35	3	0	0	0	0
	6	0	0	0	0
	9	0	0	0	0
	12	0.43	0	3.77	0
	15	9.32	0	81.78	0
	18	1.65	0	14.45	0
	21	0	0	0	0
	24	0	299	0	33.67
	27	0	589	0	66.33
	30	0	0	0	0
0.40	3	0	0	0	0
	6	0	0	0	0
	9	0	0	0	0
	12	4.24	0	35.75	0
	15	7.58	0	63.92	0
	18	0.04	0	0.33	0
	21	0	310	0	36.11
	24	0	548	0	63.89
	27	0	0	0	0
	30	0	0	0	0
0.45	3	0	0	0	0
	6	0	0	0	0
	9	0	0	0	0
	12	9.77	0	88.96	0
	15	1.21	0	11.04	0
	18	0	120	0	14.50
	21	0	710	0	85.50
	24	0	0	0	0
	27	0	0	0	0
	30	0	0	0	0
0.50	3	0	0	0	0
	6	0	0	0	0
	9	0	0	0	0
	12	9.81	0	90.35	0
	15	1.05	0	9.65	0
	18	0	133	0	15.53
	21	0	726	0	84.47
	24	0	0	0	0
	27	0	0	0	0
	30	0	0	0	0

Appendix No.1 The Li content of elution fraction in matrix loading test

Comparing the Li content in every elution fraction to see how the matrix loading (10% to 30%) separation between the Li and Na.

Matrix loading (%)	Elution fraction (mL)	Li (ng)	Na (ng)	Li (%)	Na (%)
10	3	0	0	0	0
	6	0	0	0	0
	9	0	0	0	0
	12	0	0	0	0
	13	0	0	0	0
	14	0.50	0	3.94	0
	15	2.19	0	17.30	0
	16	4.46	0	35.18	0
	17	4.01	0	31.66	0
	18	1.36	0	10.73	0
	19	0.15	0	1.19	0
	20	0	0	0	0
	21	0	0	0	0
	24	0	14	0	0.58
	27	0	818	0	34.41
30	0	15.45	0	65.01	
15	9	0	0	0	0
	12	0.21	0	1.07	0
	15	10.07	0	50.97	0
	18	9.09	0	46.02	0
	21	0.38	0	1.94	0
	24	0	245	0	6.87
	27	0	2025	0	56.72
30	0	1300	0	36.00	
20	3	0	0	0	0
	6	0	0	0	0
	7	0	0	0	0
	8	0	0	0	0
	9	0	0	0	0
	10	0	0	0	0
	11	0.03	0	0.12	0
	12	1.02	0	4.00	0
	13	4.52	0	17.81	0
	14	8.51	0	33.50	0
	15	7.78	0	30.66	0
	16	3.08	0	12.11	0
	17	0.45	0	1.78	0
	18	0	0	0	0
	19	0	0	0	0
20	0	0	0	0	
21	0	4	0	0.07	
22	0	112	0	2.10	

The table continued

Matrix loading (%)	Elution fraction (mL)	Li (ng)	Na (ng)	Li (%)	Na (%)
	23	0	424	0	7.94
	24	0	956	0	17.88
	25	0	1334	0	24.95
	26	0	1213	0	22.68
	27	0	794	0	14.84
	28	0	339	0	6.35
	29	0	158	0	2.96
	30	0	13	0	0.24
25	9	0.09	0	0.25	0
	12	12.61	0	35.96	0
	15	21.36	0	60.91	0
	18	1.01	0	2.88	0
	21	0	519	0	7.90
	24	0	4029	0	61.39
	27	0	2016	0	30.71
	30	0	0	0	0
30	9	0.50	0	1.28	0
	12	19.24	0	49.59	0
	15	18.85	0	48.59	0
	18	0.21	0	0.54	0
	21	0	1866	0	23.23
	24	0	5342	0	66.51
	27	0	824	0	10.26
	30	0	0	0	0

Appendix No.3 The Li content of elution fraction in low matrix loading test from the regenerated column.

Comparing the Li content in every elution fraction to see how the matrix loading (1% and 2%) separation between the Li and Na using the regenerated column

Matrix loading (%)	Elution fraction (mL)	Li (ng)	Na (ng)	Li (%)	Na (%)
1	3	0.11	18.47	3.21	5.75
	6	0.16	11.96	4.48	3.73
	9	0.22	10.83	6.46	3.37
	10.5	0.36	14.14	10.40	4.40
	12	0.41	35.36	11.79	11.02
	13.5	0.11	4.12	3.17	1.28
	15	0.10	2.38	2.95	0.74
	16.5	0.31	2.68	8.92	0.84
	18	0.61	43.85	17.70	13.66
	19.5	0.53	1.18	15.24	0.37
	21	0.11	6.26	3.15	1.95
	22.5	0.00	3.26	0.11	1.02
	24	0.01	2.76	0.41	0.86
	25.5	0.24	18.23	7.04	5.68
	27	0.03	38.78	0.77	12.08
	28.5	0.04	36.70	1.28	11.43
	30	0.10	69.99	2.92	21.81
2	3	0.09	112.05	2.30	18.19
	6	0.16	14.85	3.98	2.41
	9	0.20	17.93	5.05	2.91
	10.5	0.10	6.11	2.54	0.99
	12	0.19	21.65	4.83	3.51
	13.5	0.12	24.34	3.02	3.95
	15	0.17	41.89	4.37	6.80
	16.5	0.56	10.39	13.95	1.69
	18	1.50	15.80	37.49	2.57
	19.5	0.75	28.35	18.64	4.60
	21	0.06	27.22	1.59	4.42
	22.5	0.05	4.56	1.17	0.74
	24	0	3.54	0	0.57
	25.5	0.01	12.51	0.36	2.03
	27	0.03	24.51	0.71	3.98
	28.5	0	82.95	0	13.47
	30	0	167.29	0	27.16

Appendix No.4 The Li content of elution fraction in low matrix loading test from the fresh column.

Comparing the Li content in every elution fraction to see how the matrix loading (1% and 2%) affects separation between the Li and Na using the fresh column.

Matrix loading (%)	Elution fraction (mL)	Li (ng)	Na (ng)	Li (%)	Na (%)
1	15	0.03	0	2.36	0
	16	0.25	0	20.58	0
	17	0.38	0	31.30	0
	18	0.33	0	27.43	0
	19	0.16	0	13.29	0
	20	0.05	0	3.86	0
	21	0.01	0	1.17	0
	24	0	0	0	0
	27	0	13	0	12.38
	30	0	92	0	87.62
2	15	0.05	0	2.31	0
	16	0.50	0	21.93	0
	17	0.66	0	29.11	0
	18	0.57	0	24.94	0
	19	0.35	0	15.49	0
	20	0.13	0	5.72	0
	21	0.01	0	0.51	0
	24	0	0	0	0
	27	0	67	0	24.11
	30	0	212	0	75.89

Appendix No.5 The Li content of elution fraction loaded on 10% matrix loading sample solution with 2x and 3 x Li.

Comparing the Li content in every elution fraction to see how the Li content in the sample solution affects separation between the Li and Na using the fresh column.

Matrix Loading (%)	Li Loading	Elution fraction (mL)	Li (ng)	Na (ng)	Li (%)	Na (%)
10	x2	3.00	0	0	0	0
		6.00	0	0	0	0
		9.00	0	0	0	0
		10.50	0	0	0	0
		12.00	0.03	0	0.14	0
		13.00	0.27	0	1.13	0
		14.00	1.38	0	5.72	0
		15.00	4.09	0	16.95	0
		16.00	7.55	0	31.34	0
		17.00	7.23	0	29.99	0
		18.00	2.96	0	12.28	0
		19.00	0.50	0	2.08	0
		20.00	0.06	0	0.26	0
		21.00	0.02	0	0.09	0
		24.00	0	14	0	0.64
		27.00	0	730	0	34.17
30.00	0	1391	0	65.19		
20	x2	3.00	0	0	0	0
		6.00	0	0	0	0
		7.00	0	0	0	0
		8.00	0	0	0	0
		9.00	0.00	0	0	0
		10.00	0.05	0	0.10	0
		11.00	0.54	0	1.13	0
		12.00	2.59	0	5.41	0
		13.00	8.14	0	16.99	0
		14.00	14.49	0	30.25	0
		15.00	13.76	0	28.72	0
		16.00	6.57	0	13.72	0
		17.00	1.57	0	3.27	0
		18.00	0.19	0	0.40	0
		19.00	0.00	0	0	0
		20.00	0	0	0	0
21.00	0	26	0	0.55		
24.00	0	1313	0	27.53		
27.00	0	2833	0	59.41		
30.00	0	597	0	12.52		
10	x3	3.00	0	0	0	0
		6.00	0	0	0	0

The table continued

Matrix Loading (%)	Li Loading	Elution fraction (mL)	Li (ng)	Na (ng)	Li (%)	Na (%)
		9.00	0	0	0	0
		10.50	0	0	0	0
		12.00	0.01	0	0	0
		13.00	0.43	0	1.21	0
		14.00	2.37	0	6.65	0
		15.00	7.33	0	20.58	0
		16.00	12.38	0	34.79	0
		17.00	9.56	0	26.86	0
		18.00	3.04	0	8.54	0
		19.00	0.44	0	1.24	0
		20.00	0.03	0	0.10	0
		21.00	0	0	0	0
		24.00	0	6	0	0.32
		27.00	0	821	0	39.54
		30.00	0	1249	0	60.14
		3.00	0	0	0	0
		6.00	0	0	0	0
		7.00	0	0	0	0
		8.00	0	0	0	0
		9.00	0	0	0	0
		10.00	0.10	0	0.14	0
		11.00	0.80	0	1.10	0
		12.00	3.78	0	5.20	0
		13.00	12.06	0	16.57	0
20	x3	14.00	22.16	0	30.44	0
		15.00	21.65	0	29.74	0
		16.00	9.97	0	13.70	0
		17.00	2.02	0	2.77	0
		18.00	0.22	0	0.30	0
		19.00	0.02	0	0	0
		20.00	0	0	0	0
		21.00	0	17	0	0.35
		24.00	0	1166	0	24.53
		27.00	0	2982	0	62.72
		30.00	0	589	0	12.39
		3.00	0.05	0	0.37	0
		6.00	0.05	0	0.35	0
		9.00	0.05	0	0.41	0
		10.50	0.05	0	0.41	0
		12.00	0.07	0	0.54	0
10	x1	13.00	0.21	0	1.61	0
		14.00	0.82	0	6.22	0
		15.00	2.20	0	16.66	0
		16.00	3.88	0	29.39	0
		17.00	3.56	0	26.98	0
		18.00	1.52	0	11.51	0

The table continued

Matrix Loading (%)	Li Loading	Elution fraction (mL)	Li (ng)	Na (ng)	Li (%)	Na (%)
		19.00	0.31	0	2.37	0
		20.00	0.06	0	0.49	0
		21.00	0.03	0	0.22	0
		24.00	0.18	24	1.38	1.22
		27.00	0.07	1281	0.56	64.30
		30.00	0.07	687	0.52	34.48

Appendix No.6 The Li content of elution fraction loaded on sample solution digested in 0.05 M and 0.1 M HCl.

Comparing the Li content in every elution fraction to see how acid concentration in sample solution affects separation between the Li and Na using the fresh column.

HCl concentration in sample solution (M)	Elution fraction (mL)	Li (ng)	Na (ng)	Li (%)	Na (%)
0.05	12	0	0	0	0
	13	0.05	0	0.39	0
	14	0.52	0	3.77	0
	15	1.82	0	13.24	0
	16	3.88	0	28.26	0
	17	4.65	0	33.84	0
	18	2.68	0	19.50	0
	19	0.65	0	4.75	0
	20	0.06	0	0.41	0
	21	0	0	0	0
	24	0	19	0	0.78
	27	0	689	0	28.74
	30	0	1690	0	70.48
0.1	12	0	0	0	0
	13	0.08	0	0.59	0
	14	0.76	0	5.80	0
	15	2.95	0	22.67	0
	16	4.99	0	38.27	0
	17	3.84	0	29.49	0
	18	1.13	0	8.66	0
	19	0.12	0	0.92	0
	20	0	0	0	0
	21	0	0	0	0
	24	0	40	0	1.49
	27	0	1105	0	41.09
	30	0	1544	0	57.41

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Development of Li column chemistry procedure for calcium carbonate material

(title of thesis)

supervised by _Päärn Paiste

(supervisor's name)

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25/05/2021

INFORMATION SHEET

Development of Li column chemistry procedure for calcium carbonate material

The main objective of the study was to develop a relatively fast and robust column to isolate Li from the matrix components in solutions prepared from carbonate materials. Four parameters, eluent concentration, matrix loading, Li and acid concentration in sample solutions, were used to evaluate the column's efficiency and robustness. The thesis results show that Li and acid concentration in the sample solution do not affect the Li isolation, but the elution range of higher matrix loading will shift to the smaller range. The whole eluting procedure with optimized concentration 0.3 M HCl only takes around 4 hours. The δ^7 Li values with uncertainties (2σ) of samples prepared using the developed set-up were highly consistent with the reference values and the comparative measurement.

Keywords: carbonate matrix, Li ion exchange column, δ^7 Li

CERCS code: P300 Analytical chemistry

INFOLEHT

Li-kolonn keemilise protseduuri väljatöötamine kaltsiumkarbonaatmaterjalile

Uuringu põhieesmärk oli välja töötada suhteliselt kiire ja robustne kolonn Li eraldamiseks maatriksi komponentidest karbonaatmaterjalidest valmistatud lahustes. Kolonn efektiivsuse ja robustsuse hindamiseks kasutati 4 parameetrit: eluendi kontsentratsioon, kolonni koormamine ning Li ja happe kontsentratsioon proovilahustes. Töö tulemused näitavad, et Li ja happe kontsentratsioon proovilahuses ei mõjuta Li eraldamist, kuid kolonni suurem koormus mõjutab elueerimisvahemiku. Kogu protseduur, elueerides optimeeritud kontsentratsiooniga 0,3 M HCl, võtab aega umbes 4 tundi. Välja töötatud kolonniga töödeldud proovidest mõõdetud δ^7 Li väärtused koos määramatustega (2σ) ühtivad referentsväärtuste ja võrdlusmõõtmiste tulemustega

Märksõnad: karbonaatne maatriks, Li ionivahetuskolonn, δ^7 Li

CERCS: P300 analüütiline keemia