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A Simple and Efficient Approach to Determine Lithium and Multi-Elements in Lithium-Bearing Clay Minerals through a Partial Extraction Using Ammonium Hydrogen Fluoride

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Abstract: Lithium (Li) is vital to the world economy as an irreplaceable element in new-generation sustainable energy applications. Quantifying Li levels in clay minerals, a key new resource, supports extensive mineralization surveys. The major limitation in these analyses is complete decomposition, which often requires the use of strong acids and is labor-intensive, particularly in batch processing. This paper presents a partial extraction strategy for quantifying Li and multiple elements, employing ammonium hydrogen fluoride to extract from clay minerals while avoiding the use of various strong acids. Following extraction, the efficiency for Li reaches 98.61%, with values ranging from 62.68% to 91.43% for multiple elements including three major elements (Ca, Fe, Mg) and eleven trace elements (Be, Co, Cr, Cu, Ga, Mn, Ni, P, Rb, Sr, V), demonstrating favorable precision (RSD below 7.34%). This approach offers a promising tool for a simple and efficient batch analysis in the survey of mineralization in Li-bearing clay deposits.

Keywords: lithium; lithium-bearing clay; partial extraction; ammonium hydrogen fluoride

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1. Introduction

Lithium (Li), the lightest solid element (ρ = 0.53 g cm^{-3} at 20 °C), exhibits the smallest ionic radius among all alkali metals and the highest electrochemical potential [1]. Li is crucial to the world economy due to its widespread applications in various industries [2], emerging as an irreplaceable element for many high-tech applications, especially in new-generation sustainable energy technologies such as high-capacity energy storage and new-energy vehicles [3,4]. Consequently, demand for Li continues to grow, putting additional pressure on the Li mining industry. According to the United States Geological Survey (USGS), the identified global Li resources exceeded 86 Mt in 2020, with annual Li production reaching 82,000 tons. Brine and pegmatite are the dominant economic lithium deposits, which support 93% of the global demand [5–7]. However, mining companies display great eagerness to explore Li deposits due to high profit as the price of spot-battery-grade lithium carbonate is near RMB 100 kilo for each ton.

The occurrence of Li in clay minerals, predominantly in kaolinite, has been suggested as a potential new resource [8,9]. Therefore, quantifying Li levels in clay minerals is critical when surveying for mineralization. To convert a solid mineral sample to an adequate homogeneity solution, which is suitable for an accurate and stable chemical analysis by an analytical instrument, digestion is the most ordinary sample pretreatment. Various digestion methods are used in a routine analysis of geological samples across different laboratories, such as open vessel acid digestions, microwave dissolution [10], and high-pressure (bomb) digestions [11]. Complete decomposition is the prerequisite for a geological sample chemical analysis, but it is limited by environmental and efficiency issues considering a variety of strong inorganic acids' consumption, which is a corrosive and labor-intensive complex process, especially in a batch analysis. For example, decomposition by an open vessel requires four types of strong inorganic acids, namely hydrofluoric acid (HF), hydrochloric acid (HCl), nitric acid (HNO_3), and perchloric acid ($HClO_4$), which are operator-endangering and environmentally polluting. Owing to the similar decompositional capacity with HF and higher boiling point (239.5 °C), a rapid and simple digestion technique using solid ammonium bifluoride (NH_4HF_2) [12–14] has been developed to digest refractory geological materials such as zircon for 3 h at 230 °C [15]. NH_4HF_2 offers several advantages, including efficiency, safety, simple operation, and low blanks [16–19], importantly avoiding the use of corrosive and toxic HF acid typically used in traditional acid digestion.

Unlike academic research, the investigation of a target element with some associated elements instead of all elements in mineral samples is more economic and time-efficient. Partial extractions, which control the dissolution of specific phases used to investigate the distribution of target elements, have been widely employed in geochemical exploration. It is imperative to establish a simple and efficient approach applicable to the newly concerned Li-bearing-clay-type minerals. This study developed a simple partial extraction approach using NH_4HF_2 for Li and multiple associated elements. A detailed comparison of the different extraction behaviors of Li was conducted, and the extraction efficiency and precision of the established approach were verified, showcasing its effectiveness in a batch analysis of mineral surveying targeting Li-bearing clay minerals.

2. Materials and Methods

2.1. Materials and Reagents

Citric acid ($C_6H_8O_7$), ammonium chloride (NH_4Cl), ammonium sulfate ($(NH_4)_2SO_4$), ferric chloride ($FeCl_3$), ferric nitrate ($Fe(NO_3)_3$), and ammonium hydrogen fluoride ($(NH_4)HF_2$) were all purchased from Sinopharm Chemical Reagent (Shanghai, China). Ferric sulfate ($Fe_2(SO_4)_3$) was purchased from Kemiou Chemical Reagent (Tianjin, China). HF, HCl, HNO_3, $HClO_4$ and sulfuric acid (H_2SO_4) were purchased from Zhongtian Chem (Wuhan, China). Except for HNO_3 and $(NH_4)HF_2$, which are guaranteed reagent grades, all other reagents are of analytical grades. All water used was deionized. A Li standard solution in HNO_3 (1000 $\mu g\ mL^{-1}$), and multi-elements' standard solution (1000 $\mu g\ mL^{-1}$) were purchased from Guobiao (Beijing, China) Testing & Certification (GBTC, Beijing, China). National reference materials GBW07152 [20] and GBW07735 [21] were purchased from the National Sharing Platform for Reference Materials (Beijing, China).

2.2. Sample Digestion

Li-bearing clay minerals were collected from Nanzhang (Xiangyang, China) and their original photograph is shown in Figure 1. The clay minerals were milled to −200 mesh (<74 μm) using GSXX-4 Planetary Ball Mills (Huaxiang Geological Environment Testing Technology, Wuhan, China).

For the total content quantification of multiple elements in mineral samples, the Li-bearing clay mineral was fully digested by an open vessel acid digestion method. Briefly, 0.1 g of the sample was accurately weighed into a 30 mL Teflon vessel, and samples were wetted with several drops of water. In total, 5 mL of HF, 3 mL of HCl, 2 mL of HNO_3, and 1 mL of $HClO_4$ were added and left overnight at room temperature. The vessel was then slowly heated to 120 °C for pre-digestion and increased to 200 °C to remove fluorine. The residue in the vessel was extracted with 1 mL of HCl to obtain a sample solution. This solution was then diluted with water to achieve a dilution factor of 100 for measurement.

Figure 1. The original photograph of Li-bearing clay minerals.

2.3. ICP-OES and ICP-MS Analysis

Thirteen elements, namely Li, Al, Ca, Cr, Fe, K, Mg, Mn, Na, P, Sr, Ti, and V, were analyzed using an iCAP™ 7400 ICP-OES analyzer (Thermo Fisher Scientific, Waltham, MA, USA). The parameters were as follows: nebulizer gas pressure, 0.25 MPa; auxiliary gas flow, 0.5 L/min; coolant gas flow, 12 L/min; RF power, 1100 W; vertical observation height, 12 mm; analysis pump speed, 50 rpm; long-wave exposure time, 7 s; and short-wave exposure time, 12 s. Relevant wavelengths are summarized in Table 1. Data acquisition was performed using iTEVA iCAP software (version 2.8.0.96, Thermo Fisher Scientific, Waltham, MA, USA).

Table 1. Wavelengths chosen in ICP-OES for several elements in Li-bearing clay minerals.

Elements	**Wavelength (nm)**
Li	670.7
Al	394.4
Ca	318.1
Cr	267.7
Fe	259.9
K	766.4
Mg	279.0
Mn	257.6
Na	589.5
P	214.9
Sr	407.7
Ti	337.2
V	292.4

Seven elements, namely Be, Co, Cs, Cu, Ga, Ni, and Rb, were analyzed using a Thermo Scientific XSERIES 2 ICP-MS (Thermo Fisher Scientific, Waltham, MA, USA). The parameters were as follows: nebulizer gas flow, 0.88 L/min; auxiliary gas flow, 0.8 L/min; coolant gas flow, 14 L/min; RF power, 1300 W; analysis pump speed, 50 rpm; sample cone, 1.0 mm; and skimmer cone, 0.8 mm. Relevant isotopes are summarized in Table 2. Re (2 ng/mL) and Rh (2 ng/mL) in 2% nitric acid were used as internal standard solutions. Data acquisition was performed using PlasmaLab software (version 2.6.1.335, Thermo Fisher Scientific, Waltham, MA, USA).

Table 2. Isotopes chosen in ICP-MS for several elements in Li-bearing clay minerals.

Elements	**Isotopes**
Be	^{9}Be
Co	^{59}Co
Cs	^{133}Cs
Cu	^{63}Cu
Ga	^{71}Ga
Ni	^{60}Ni
Rb	^{85}Rb

2.4. XRD Analysis

The XRD patterns of the Li-bearing clay minerals were obtained using a Bruker D8 FOCUS X-ray diffractometer (Bruker, Billerica, MA, USA) with Cu irradiation in the 2θ range of 5–60°, operating at 40 kV and 40 mA.

3. Results and Discussion

3.1. Total Li and Multi-Elements' Content and XRD Spectrum of Li-Bearing Clay Minerals

The XRD spectrum of the Li-bearing clay minerals revealed that the primary mineral composition is kaolinite (represent as red line), a typical clay-type mineral (Figure 2A). The total content of major and trace elements in the Li-bearing clay minerals, obtained by a full digestion method using an acid mixture, is presented in Table 3. The results showed that the Li_2O grade of these minerals is 0.49%, with the basic elemental composition primarily consisting of SiO_2 and Al_2O_3, while other major elements are below 1.35%. These findings suggest that Li-bearing clay minerals have significant potential as a Li deposit.

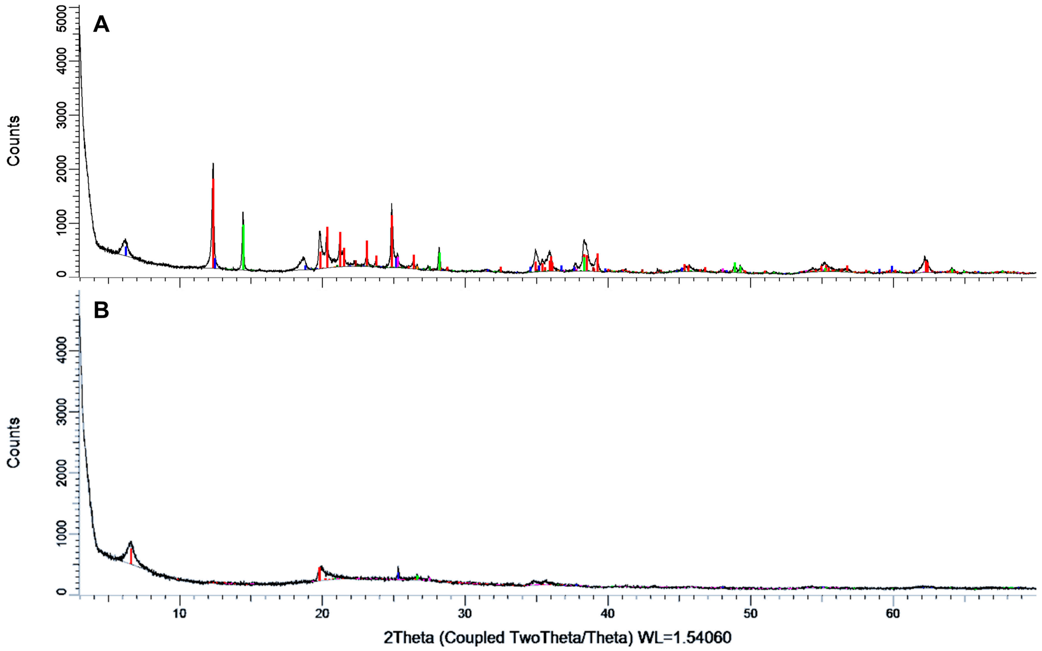

Figure 2. The XRD spectrum of Li-bearing clay minerals before (**A**) and after (**B**) roasting. Red line, Kaolinite.

Table 3. Major and trace elements' contents in Li-bearing clay minerals.

Major Elements *	Content (%)	Trace Elements	Content (μg/g)
Li_2O	0.49	Be	3.43
Al_2O_3	40.51	Co	9.65
CaO	0.21	Cr	101.15
TFe_2O_3	1.10	Cs	11.07
K_2O	0.61	Cu	29.80
MgO	1.03	Ga	41.57
Na_2O	0.22	Mn	15.24
SiO_2	39.53	Ni	94.30
TiO_2	1.35	P	285.10
		Pb	28.60
		Rb	21.64
		Sr	139.64
		V	180.74
		Zn	18.70

* Major elements are presented in oxide form.

3.2. Direct Leaching of Li-Bearing Clay Minerals

Routine digestion methods such as open vessel acid digestion, microwave dissolution, alkali fusion, and high-pressure (bomb) digestion are capable of decomposing several geological materials [22]. However, these methods are labor-intensive and time-consuming and can cause environmental damage due to the emission of acid gases during a batch analysis. Given the simple elemental and mineral composition of clay-type minerals, this research aimed to establish an extraction method that avoids prolonged digestion times and extensive use of acids in a batch analysis.

Ammonium-salt-based leaching techniques have been widely used in the weathering crusts for rare earth element mining [23]. Five salt-based leaching solutions, including two ammonium-salt-based solutions (NH_4Cl, $(NH_4)_2SO_4$) and three ferric-salt-based solutions ($FeCl_3$, $Fe_2(SO_4)_3$, $Fe(NO_3)_3$), were assessed with $C_6H_8O_7$ and H_2SO_4 for directly leaching Li from minerals. In total, 5 g of clay minerals was agitated (160 rpm) with 25 mL of a leaching solution (10%, w/v) at 25 °C for 2 h. The results indicated that the recovery efficiency of all these leaching solutions was lower than 0.15% (Figure 3A), demonstrating that direct leaching barely extracts Li from clay minerals. It can be deduced that Li-bearing clay minerals, which are phyllosilicates with crystal structures primarily composed of two tetrahedral sheets and an octahedral sheet [9], restrict the extraction of Li due to Li^+ and other cations substituting for Al^{3+}, Fe^{3+}, and Mg^{2+} in octahedral sites.

A roasting process at 600 °C for 2 h was performed on the Li-bearing clay prior to leaching to alter the mineral structure. It was found that the recovery efficiency of all leaching solutions significantly increased under the same leaching conditions (Figure 3B), with a maximum of nearly 90%. The XRD spectrum showed that the mineral structure was completely changed after roasting (Figure 2B). Research indicated that a dehydroxylation reaction occurred, and gases including CH_2, CH_4, C_3H_4, C_6H_5, and C_8H_9 were evolved during the roasting process, transforming $AlO_4(OH)_2$ octahedra into AlO_4 tetrahedra due to the reaction between the reductive gases and the residual oxygen in AlO_5, which rendered the kaolinite amorphous [24].

Owing to the highest recovery efficiency of H_2SO_4, the concentration of the acid was further optimized using three different inorganic acids (HCl, HNO_3, and H_2SO_4) at five levels (10%, 20%, 30%, 40%, 50%, v/v). The leaching efficiency increased with the acid concentration, reaching a plateau at 40% (v/v) for all three acids (Figure 4).

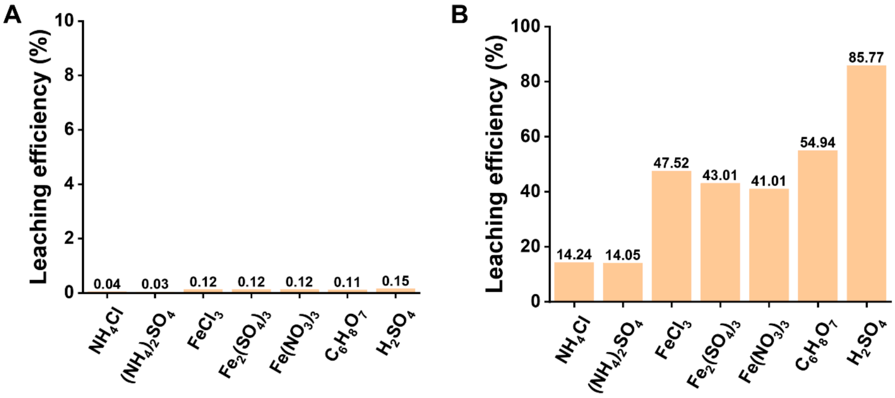

Figure 3. Leaching efficiency of direct leaching before (**A**) and after (**B**) roasting.

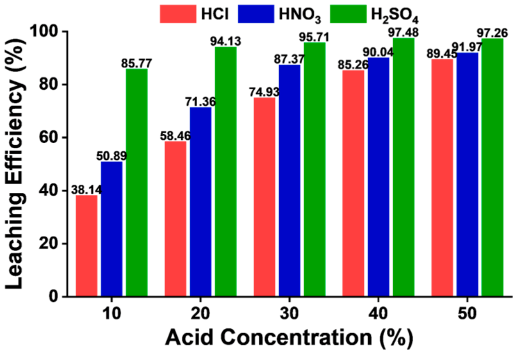

Figure 4. Optimization of leaching acid type with diverse concentrations.

3.3. Partial Extraction of Li-Bearing Clay Minerals

Although the maximum recovery efficiency of H_2SO_4 leaching is nearly 98% after roasting, using a furnace and high concentration of strong acids is inconvenient and hazardous in a batch analysis. To avoid using a furnace and to reduce the concentration of strong acids, a partial extraction approach was established using $(NH_4)HF_2$, which offers advantages such as efficiency, safety, simple operation, and low blanks [12]. In this study, a combination of $(NH_4)HF_2$ and H_2SO_4 was employed to establish a partial extraction method for Li-bearing clay minerals.

A mixture of $(NH_4)HF_2$ and H_2SO_4 was compared with the separate use of $(NH_4)HF_2$ and H_2SO_4 for partially extracting Li from minerals. In total, 5 g of clay minerals was agitated (160 rpm) with 25 mL of an extracting solution (10%, w/v) at 25 °C for 2 h. The results found that the recovery efficiency of the combined $(NH_4)HF_2$ and H_2SO_4 solution was significantly higher than when using $(NH_4)HF_2$ and H_2SO_4 separately (Figure 5A). Due to the higher boiling point (239.5 °C) of $(NH_4)HF_2$ compared to conventional acids such as HF, HNO_3, and HCl, an elevated digestion temperature in open vessels is possible, enabling the decomposition of refractory phases [15]. The extracting solution was then heated to 240 °C on a hotplate for 3 h until the acid vapor was completely removed. With heating, the acid concentration was further optimized using two different strong inorganic acids (HCl and H_2SO_4) at three levels (5%, 10%, 20%, v/v). The extraction efficiency significantly increased 3.42-fold after heating and also increased with the acid concentration (Figure 5B). However, due to the dangers associated with using high concentrations of strong acids, further increasing the acid concentration would cause toxic and environmental pollution in a batch analysis. Moreover, the amount of $(NH_4)HF_2$ in the extraction solution was optimized from 1 g to 10 g. The recovery efficiency increased with the amount of $(NH_4)HF_2$, reaching a plateau at 8 g, where the maximum extraction efficiency was 98.61% (Figure 5C). However, due to the production of insoluble fluoride, further increasing the amount of

$(NH_4)HF_2$ caused a certain degree of recovery reduction. The vibrating or extracting time was also evaluated, but the results showed no significant difference between varied times

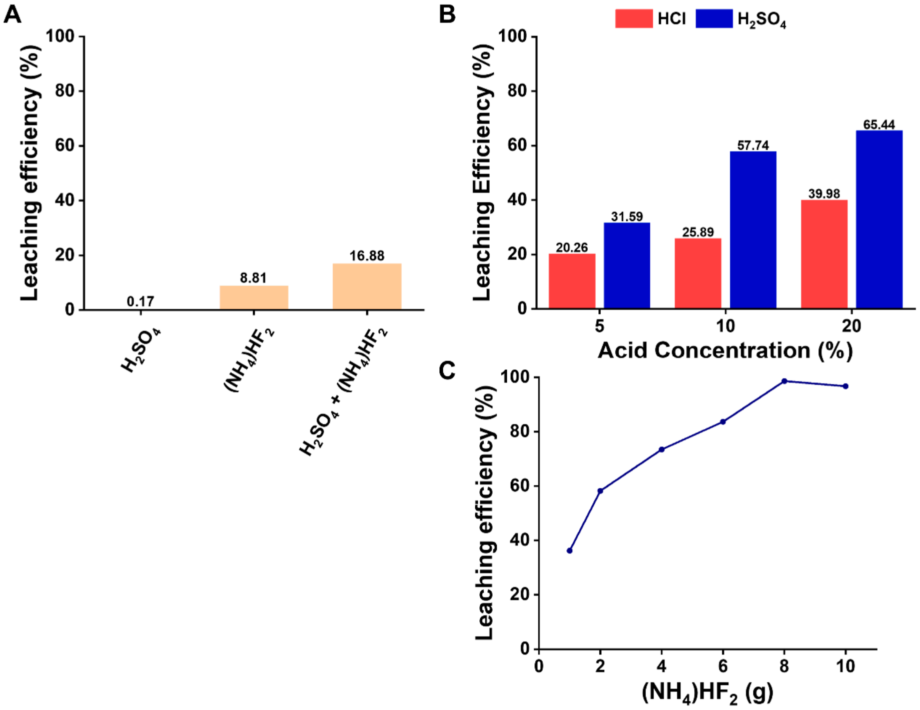

Figure 5. Optimization of partial extraction conditions. (**A**) Extraction without heat. (**B**) Types and concentration of acids. (**C**) Amount of $(NH_4)HF_2$.

3.4. Extraction Efficiency of Multi-Elements

Collectively, the optimized conditions for partial extraction were as follows: 2 g of clay mineral samples was accurately weighed with 8 g of $(NH_4)HF_2$ in 10 mL of H_2SO_4 (20%, v/v), then agitated under 25 °C for 1 h. The extraction solution was heated at 240 °C on a hotplate for 3 h until the acid vapor was completely removed. The residue was extracted with 1 mL of HCl to obtain a sample solution. The sample solution was then diluted with water to achieve a dilution factor of 250 for ICP-OES measurement and 2500 for ICP-MS measurement. Under the optimized conditions, the extraction efficiency of multi-elements, including 4 major elements (Al, Ca, Fe, Mg) and 12 trace elements (Be, Co, Cr, Cs, Cu, Ga, Mn, Ni, P, Rb, Sr, V), was higher than 60%, except Al and Cs, which were 50.47 and 51.03, respectively (Table 4). This indicates the effective capability of this partial extraction approach for multi-elements in Li-bearing clay minerals.

Table 4. Extraction efficiency of major and trace elements in Li-bearing clay minerals by partial extraction approach.

Elements	Extraction Efficiency (%)	Elements	Extraction Efficiency (%)
Al	50.47	Ga	62.89
Be	86.86	Mg	75.94
Ca	90.43	Mn	91.32
Co	78.82	Ni	77.06
Cr	65.01	P	88.73
Cs	51.03	Rb	64.78
Cu	62.68	Sr	73.81

3.5. The Reproducibility of Partial Extraction

Owing to only quantifying part of the element content, but this shall reflect the total level of mineral ores, the reproducibility of a partial extraction approach should stay consistent. For industrial application potential evaluation, the reproducibility of the proposed method was thoroughly evaluated by assessing the relative standard deviation (RSD). As depicted in Table 5, the calculated RSDs were consistently below 7.34%, which underscored the attained precision of the proposed method for the extraction of Li and multi-elements.

Table 5. Reproducibility for partial extraction of multi-elements in Li-bearing clay minerals.

Elements	Li	Al	Be	Ca	Co	Cr	Cs	Cu	Fe
Precision (RSD, %; *n* = 6)	2.12	5.53	7.34	1.97	4.73	3.12	6.49	5.00	2.40
Elements	Ga	Mg	Mn	Ni	P	Rb	Sr	V	
Precision (RSD, %; *n* = 6)	4.42	2.27	2.08	3.73	1.63	5.67	2.69	3.72	

4. Conclusions

This study established a partial extraction approach using $(NH_4)HF_2$ to elucidate a range of elements involved in Li, major elements, and trace elements. The utilization of $(NH_4)HF_2$ has significantly enhanced the extraction of Li in Li-bearing clay minerals without the need for roasting and the use of high-concentration strong acids. This approach exhibits favorable precision, with an RSD below 7.34%. Overall, this method demonstrates broad application and holds promising potential for widespread adoption in batch analyses of Li-bearing clay minerals.

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Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Tarascon, J.-M. Is lithium the new gold? *Nat. Chem.* **2010**, *2*, 510. [CrossRef] [PubMed]
2. Grey, C.P.; Hall, D.S. Prospects for lithium-ion batteries and beyond—A 2030 vision. *Nat. Commun.* **2020**, *11*, 6279. [CrossRef] [PubMed]
3. Wu, F.; Maier, J.; Yu, Y. Guidelines and trends for next-generation rechargeable lithium and lithium-ion batteries. *Chem. Soc. Rev.* **2020**, *49*, 1569–1614. [CrossRef] [PubMed]
4. Kim, T.; Song, W.; Son, D.-Y.; Ono, L.K.; Qi, Y. Lithium-ion batteries: Outlook on present, future, and hybridized technologies. *J. Mater. Chem. A* **2019**, *7*, 2942–2964. [CrossRef]
5. Sanjuan, B.; Gourcerol, B.; Millot, R.; Rettenmaier, D.; Jeandel, E.; Rombaut, A. Lithium-rich geothermal brines in Europe: An up-date about geochemical characteristics and implications for potential Li resources. *Geothermics* **2022**, *101*, 102385. [CrossRef]
6. Bazamad, M.; Tangestani, M.H.; Asadi, S.; Staubwasser, M. Investigating the geochemical behavior and exploration potential of lithium in brines; A case study of Bam salt plug, Zagros Zone, southern Iran. *Sci. Rep.* **2023**, *13*, 21567. [CrossRef] [PubMed]
7. Coffey, D.M.; Munk, L.A.; Ibarra, D.E.; Butler, K.L.; Boutt, D.F.; Jenckes, J. Lithium Storage and Release From Lacustrine Sediments: Implications for Lithium Enrichment and Sustainability in Continental Brines. *Geochem. Geophys. Geosyst.* **2021**, *22*, e2021GC009916. [CrossRef]
8. Ling, K.; Wen, H.; Zhang, Q.; Luo, C.; Gu, H.; Du, S.; Yu, W. Super-enrichment of lithium and niobium in the upper Permian Heshan Formation in Pingguo, Guangxi, China. *Sci. China Earth Sci.* **2021**, *64*, 753–772. [CrossRef]
9. Zhao, H.; Wang, Y.; Cheng, H. Recent advances in lithium extraction from lithium-bearing clay minerals. *Hydrometallurgy* **2023**, *217*, 106025. [CrossRef]

10. Prasad, A.D.; Rastogi, L.; Thangavel, S.; Dash, K. A Single Step Acid Assisted Microwave Digestion Method for the Complete Dissolution of Bauxite and Quantitation of its Composition (Al_2O_3, Fe_2O_3, SiO_2, TiO_2, Cr_2O_3, MgO, MnO and V_2O_5) by ICP-AES. *Geostand. Geoanal. Res.* **2023**, *47*, 403–413. [CrossRef]
11. Zhang, W.; Hu, Z. Recent advances in sample preparation methods for elemental and isotopic analysis of geological samples. *Spectrochim. Acta Part B At. Spectrosc.* **2019**, *160*, 105690. [CrossRef]
12. Liu, H.; Hu, Z.; He, T.; Zhang, W.; Zong, K.; Luo, T.; Qiu, X.; Gao, Y.; Li, M. Evaluation of the digestion capability of ammonium bifluoride for the determination of major and trace elements in Ti-rich minerals by ICP-MS. *J. Anal. At. Spectrom.* **2023**, *38*, 1146–1154.
13. He, T.; Li, M.; Hu, Z.; Zhang, W.; Chen, H.; Wang, Z.; Liu, Y. Quantification of Cl, Br and I in Geological Materials by NH_4F Digestion: Comparison with Rapid Acid Digestion. *Geostand. Geoanal. Res.* **2023**, *47*, 155–168.
14. Zhang, C.; Zhang, W.; Hu, Z.; He, T.; Liu, Y.; Chen, H. An Improved Procedure for the Determination of Trace Elements in Silicate Rocks Using NH_4HF_2 Digestion. *Geostand. Geoanal. Res.* **2022**, *46*, 21–35.
15. Zhang, W.; Hu, Z.; Liu, Y.; Chen, H.; Gao, S.; Gaschnig, R.M. Total Rock Dissolution Using Ammonium Bifluoride (NH_4HF_2) in Screw-Top Teflon Vials: A New Development in Open-Vessel Digestion. *Anal. Chem.* **2012**, *84*, 10686–10693. [PubMed]
16. Újvári, G.; Klötzli, U.; Horschinegg, M.; Wegner, W.; Hippler, D.; Kiss, G.I.; Palcsu, L. Rapid decomposition of geological samples by ammonium bifluoride (NH_4HF_2) for combined Hf-Nd-Sr isotope analyses. *Rapid Commun. Mass Spectrom.* **2021**, *35*, e9081.
17. Magaldi, T.T.; Navarro, M.S.; Enzweiler, J. Assessment of Dissolution of Silicate Rock Reference Materials with Ammonium Bifluoride and Nitric Acid in a Microwave Oven. *Geostand. Geoanal. Res.* **2019**, *43*, 189–208.
18. O'Hara, M.J.; Kellogg, C.M.; Parker, C.M.; Morrison, S.S.; Corbey, J.F.; Grate, J.W. Decomposition of diverse solid inorganic matrices with molten ammonium bifluoride salt for constituent elemental analysis. *Chem. Geol.* **2017**, *466*, 341–351. [CrossRef]
19. Hu, Z.; Zhang, W.; Liu, Y.; Chen, H.; Gaschnig, R.M.; Zong, K.; Li, M.; Gao, S.; Hu, S. Rapid bulk rock decomposition by ammonium fluoride (NH_4F) in open vessels at an elevated digestion temperature. *Chem. Geol.* **2013**, *355*, 144–152. [CrossRef]
20. GBW07152 Lithium Ore-National Sharing Platform for Reference Materials. Available online: https://www.ncrm.org.cn/Web/OrderingEn/MaterialDetail?autoID=7200 (accessed on 30 May 2024)
21. GBW07735 Lithium Ore-National Sharing Platform for Reference Materials. Available online: https://www.ncrm.org.cn/Web/Material/Components?autoID=23421&pageIndex=5 (accessed on 30 May 2024)
22. Chen, S.; Wang, X.; Niu, Y.; Sun, P.; Duan, M.; Xiao, Y.; Guo, P.; Gong, H.; Wang, G.; Xue, Q. Simple and cost-effective methods for precise analysis of trace element abundances in geological materials with ICP-MS. *Sci. Bull.* **2017**, *62*, 277–289. [CrossRef]
23. Wang, G.; Xu, J.; Ran, L.; Zhu, R.; Ling, B.; Liang, X.; Kang, S.; Wang, Y.; Wei, J.; Ma, L.; et al. A green and efficient technology to recover rare earth elements from weathering crusts. *Nat. Sustain.* **2023**, *6*, 81–92. [CrossRef]
24. Zuo, K.; Wang, H.; Xiong, K.; Yu, C.; Cheng, H. Structural transformation and dehydroxylation of clay minerals in lithium-bearing clay. *J. Therm. Anal. Calorim.* **2022**, *147*, 13231–13237. [CrossRef]