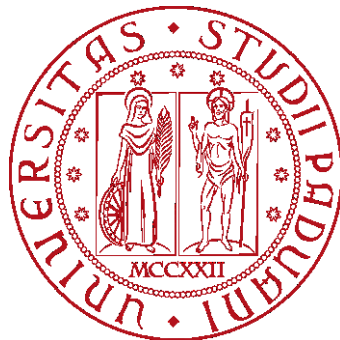




UNIVERSITÀ DEGLI STUDI DI PADOVA

SCUOLA DI SCIENZE
Dipartimento di Geoscienze
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TESI DI LAUREA IN EARTH AND CLIMATE DYNAMICS

**Design and experiments of the extraction of
critical elements and rare earth elements from
biotite-rich mine tailings**

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Dedica

For everything that brought me here, and everything that will take me further.

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Abstract:

The increasing demand for critical elements, including rare earth elements (REEs), has created the need for alternative and sustainable resource sources. Mine tailings represent a potentially valuable secondary resource due to the presence of economically important elements that remain after primary mineral processing. This thesis investigates the controlled dissolution of biotite-rich mine tailings to promote the release of selected critical elements and REEs, while limiting the dissolution of REE-bearing minerals such as monazite. The study includes the characterization of the tailings using mineralogical and chemical analytical techniques to identify the distribution and occurrence of elements.

Dissolution experiments were carried out using citric acid under controlled pH and temperature conditions to evaluate and regulate the release of critical elements and REEs into solution. The influence of experimental parameters, including pH and temperature, was assessed through the analysis of liquid samples by inductively coupled plasma mass spectrometry (ICP-MS).

The obtained results provide insights into the dissolution kinetics of the investigated elements and their extraction efficiencies from biotite-rich mine tailings. The findings provide insights into the potential of biotite-rich mine tailings as a secondary source of critical elements and REEs and highlight the importance of controlling pH and temperature to regulate mineral dissolution and element release.

Riassunto:

La crescente domanda di elementi critici, inclusi gli elementi delle terre rare (REEs), ha creato la necessità di individuare fonti di approvvigionamento alternative e sostenibili. I residui di lavorazione mineraria rappresentano una potenziale risorsa secondaria di elevato valore grazie alla presenza di elementi economicamente rilevanti che rimangono dopo il trattamento primario del minerale. La presente tesi analizza l'estrazione di elementi critici e di elementi delle terre rare da residui minerali ricchi in biotite mediante una serie di esperimenti di dissoluzione.

Lo studio comprende la caratterizzazione mineralogica e chimica dei residui minerali con l'obiettivo di identificare la distribuzione e la presenza degli elementi di interesse. Gli esperimenti di dissoluzione sono stati progettati e condotti in condizioni controllate utilizzando un acido organico per valutare il rilascio degli elementi critici e delle terre rare in soluzione. L'influenza dei principali parametri sperimentali, in particolare del pH e della temperatura, è stata valutata mediante l'analisi dei campioni liquidi con la spettrometria di massa a plasma accoppiato induttivamente.

I risultati ottenuti forniscono informazioni sul comportamento di dissoluzione degli elementi analizzati e sull'efficienza della loro estrazione dai residui minerali ricchi in biotite. Le evidenze emerse contribuiscono a una migliore comprensione del potenziale dei residui di lavorazione mineraria come fonte secondaria di materie prime critiche.

1 Introduction and motivation

1.1 Critical elements

The global transition towards low-carbon energy systems and advanced technologies has led to a rapidly increasing demand for critical raw materials (Lundaev et al., 2023; IEA, 2026). These materials are essential for the production of renewable energy technologies and a variety of advanced applications. However, many of these materials are characterized by limited geographical distribution, high import dependency and increasing supply risks, creating significant challenges for modern industries (European Commission, 2024; IEA, 2026).

Critical elements are defined as materials that are both economically important and associated with a high risk of supply disruption. Their criticality is determined by considering factors such as economic importance, supply concentration, geopolitical risks and the lack of suitable substitutes. Due to their necessary role in advanced manufacturing and clean energy technologies, the European Union regularly updates the list of critical raw materials to support resource security and promote sustainable resource management (European Commission, 2024). The supply risks associated with critical raw materials used in key technologies are illustrated in Figure 1.

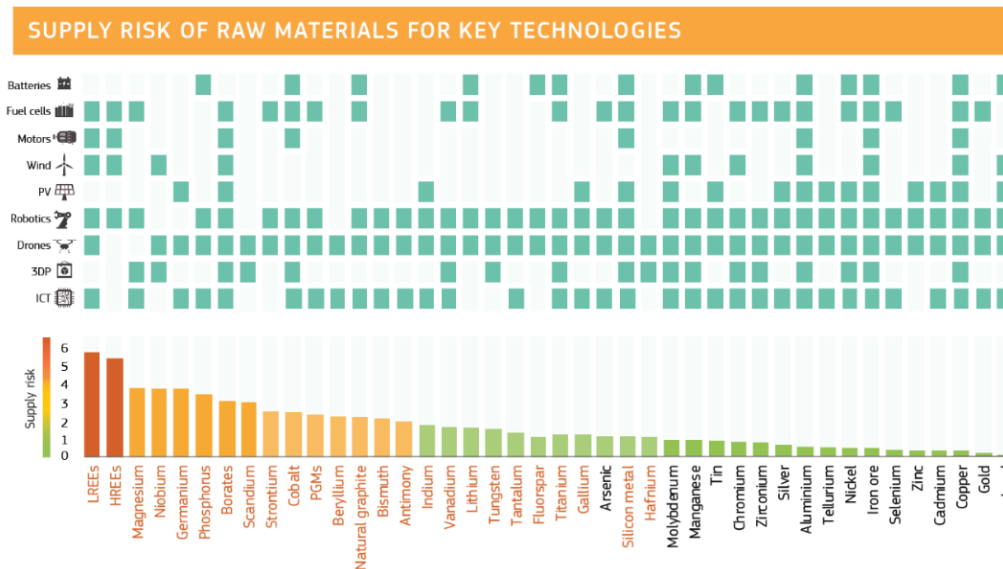


Figure 1 Supply risk of critical elements used in key technologies. Source: European Commission (2024). Information System (RMIS).

Among the critical elements, rare earth elements (REEs) are important because of their unique physical and chemical properties. REEs consist of a group of seventeen elements, including the fifteen lanthanides together with scandium (Sc) and yttrium (Y). Although these elements are relatively abundant in the Earth's crust, they rarely occur in economically exploitable concentrations and are often dispersed within different mineral phases (Balaram, 2019; IEA, 2026). The global distribution of REE reserves is illustrated in Figure 2.

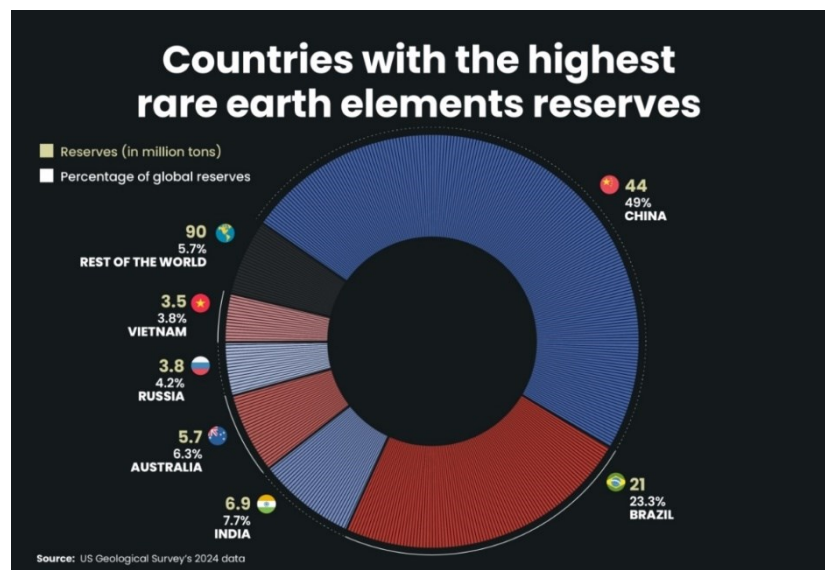


Figure 2 Global distribution of REEs reserves. Source: U.S. Geological Survey (2024).

Due to their exceptional magnetic, optical, electrical and catalytic properties, REEs are essential for a range of high-technology and low-carbon applications (Dushyantha et al., 2020; Diao et al., 2024). They are particularly important in permanent magnets used in electric vehicle motors and wind turbines, as well as in various electronic and other advanced technologies. Moreover, REEs are used in catalysts, lasers, medical equipment, glass manufacturing, and aerospace and defence applications (Dushyantha et al., 2020; Diao et al., 2024). The rapid expansion of renewable energy technologies and electrification has contributed to increasing global demand for REEs, particularly those required for permanent magnets (Diao et al., 2024).

However, there are significant environmental and economic challenges related to their extraction and processing. Primary mining operations often require large amounts of energy and chemicals, generate enormous quantities of mining waste and may cause considerable environmental impacts (Dushyantha et al., 2020; Balaram, 2019). In addition, the global supply chain for REEs is highly concentrated, increasing concerns regarding resource security and long-term availability (Dushyantha et al., 2020).

Consequently, increasing attention has been directed towards the development of more sustainable strategies for recovering critical raw materials. Secondary resources such as mine tailings have been considered as promising alternative sources of valuable elements (Kumari et al., 2018).

1.2 Mine tailings as a secondary source of critical elements

Recently, there is an increasing attention towards the development of more green strategies for recovering critical raw materials. Despite mining activities generate large quantities of waste materials (mine tailings) throughout the extraction and processing of ores, mine waste can be also considered as a secondary source of critical elements (Kinnunen et al., 2022). Recovering valuable elements from mine tailings can contribute to the circular economy and reduce the dependence on primary mining (Abbadi and Mucsi, 2024; Chowdhury and Talan, 2025). The accumulation of mine tailings presents

significant environmental and social challenges. Large tailings storage facilities occupy big land areas and may cause long-term environmental risks, including acid mine drainage, dust emissions, heavy metal contamination of soil and groundwater and dam failures. (Wibowo et al., 2023). Among these wastes, these mine tailings represent the largest volume of solid residues produced by the mining industry. Although traditionally considered as waste, many historical and active tailings deposits can still contain significant concentrations of valuable metals and critical raw materials that were not economically recoverable using the technologies available at the time of mining (Kinnunen et al., 2022; Chowdhury and Talan, 2025).

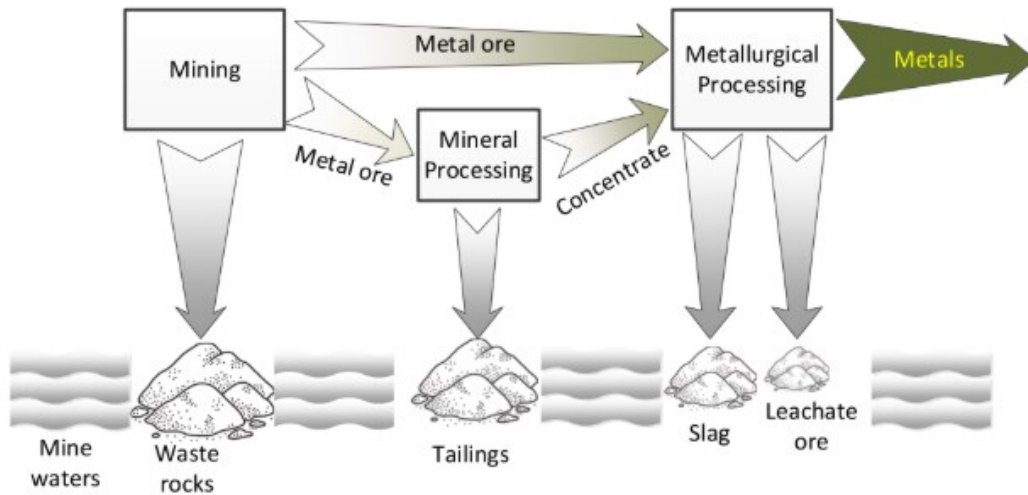


Figure 3 Origins of mineralized waste and mine tailings and their material flows throughout the mining industry. Source: Milani et al. (2025)

REEs are commonly associated with accessory minerals such as monazite, bastnäsite and xenotime, which may remain concentrated in mine tailings after the processing of the primary ore (Dushyantha et al., 2020). Advances in mineral processing, hydrometallurgy and analytical techniques have made it increasingly workable to recover these valuable elements from secondary resources. Consequently, mine tailings represent an alternative source of critical raw materials that can partially reduce dependence on primary mining (Abbadi and Mucsi, 2024).

1.3 Sustainable dissolution of minerals using organic acids

The recovery of critical elements from mine tailings requires extraction methods that are both efficient and environmentally friendly. Conventional hydrometallurgical processes commonly use strong inorganic acids, such as sulfuric, hydrochloric, and nitric acids. Although these acids can achieve high metal recovery, they are associated with high reagent consumption, equipment corrosion, and the generation of hazardous waste. Consequently, increasing attention has been directed towards the development of more environmentally friendly leaching technologies (He et al., 2025).

Organic acids have emerged as promising alternatives because they can provide acidity while also interacting with dissolved metal ions through complexation. Their potential for sustainable mineral dissolution is further supported by biological processes, in which microorganisms can produce organic acids that promote mineral dissolution through acidolysis and ligand complexation. For example, microbial activity has been shown to enhance bastnaesite dissolution through the production of organic acids, acidification of the solution, and complexation reactions (He et al., 2025).

Organic acids can also be produced from alternative and renewable carbon sources. Approaches for producing oxalic acid from CO₂ and biomass have been investigated as a potential route towards more sustainable chemical production (Schuler et al., 2021).

In addition to providing acidity for mineral dissolution, organic acids can form complexes with dissolved metal ions, consequently enhancing metal mobilization. Among the various organic acids, citric acid has received particular attention because of its strong complexing ability and its potential application in environmentally friendly metal extraction (He et al., 2025).

The effectiveness of organic-acid leaching depends on several factors, including pH, temperature, reaction time, and mineralogical composition. By carefully controlling these parameters, it is possible to influence the dissolution of specific mineral phases while minimizing the dissolution of other minerals. Such selectivity is particularly

important for the sustainable recovery of critical raw materials from mine tailings (He et al., 2025).

For these reasons, organic acids represent a promising approach for developing environmentally friendly extraction processes. However, despite their potential, the mechanisms controlling selective mineral dissolution under different conditions are still not fully understood, highlighting the need for further investigation (He et al., 2025; Potysz and Bartz, 2022). The main mechanisms involved in microbial mineral weathering are illustrated in Figure 4.

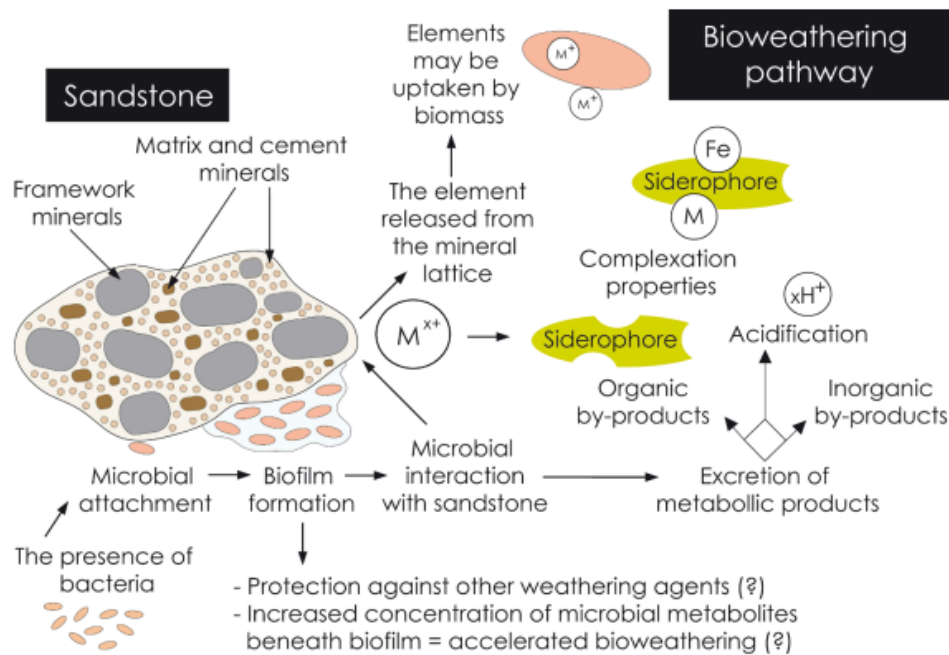


Figure 4 Schematic representation of microbial mechanisms involved in mineral weathering, including organic-acid production, acidification and complexation, leading to the release of elements from mineral phases. Source: Potysz and Bartz (2022).

1.4 Knowledge gap: extraction kinetics and mechanisms

Although previous studies have investigated the recovery of critical elements from primary and secondary resources using both inorganic and organic acids, important challenges remain in developing selective and environmentally sustainable extraction processes (Abbadi and Mucsi, 2024). In particular, organic acids have been increasingly

investigated as alternative leaching agents for the recovery of REEs from secondary resources, but their effectiveness depends strongly on the mineralogical characteristics of the material and the chemical conditions of leaching (Banerjee et al., 2022; Schuler et al., 2021).

Mineral dissolution kinetics have been extensively studied, and parameters such as pH, temperature, reaction time, mineral surface area and solution composition are known to influence dissolution rates (Brantley, 2008). For acid-promoted dissolution, the dissolution rate can be described as a function of hydrogen-ion activity and temperature. A simplified rate expression can be written as:

$$r = k(T) a_{H^+}^n$$

where r is the mineral dissolution rate, $k(T)$ is the temperature-dependent rate constant, a_{H^+} is the activity of hydrogen ions, and n is the reaction order with respect to proton activity (Appelo and Postma, 2005).

The temperature dependence of the rate constant can be described using the Arrhenius relationship and is related to the activation energy of the dissolution reaction. Mineral-specific kinetic parameters therefore result in different dissolution rates under the same pH and temperature conditions (Heřmanská et al., 2022). The authors developed a consistent database of dissolution rates for primary silicate minerals, including micas, using experimentally determined rates normalized to mineral surface area and expressed as functions of pH and temperature (Heřmanská et al., 2022). However, mineral dissolution studies have focused mainly on the dissolution rates of major rock-forming minerals and the release of their major constituent elements, comparatively less attention has been given to the dissolution and release of minor and trace elements, including critical elements and REEs. In addition, the behavior of individual minerals within complex, multi-mineral systems can differ considerably from that of isolated pure phases. This is particularly relevant for mine tailings, where critical elements may occur in accessory minerals or may be associated with other mineral phases (Abbadi and Mucsi, 2024; Banerjee et al., 2022). Therefore, understanding the relative dissolution

behavior of individual minerals under controlled leaching conditions remains important for developing selective extraction strategies.

Furthermore, relatively limited attention has been given to combining experimental dissolution data with geochemical modelling to evaluate mineral stability and dissolution behavior under the same experimental conditions. Geochemical modelling can provide additional information on mineral saturation, aqueous speciation and possible dissolution or precipitation reactions (Triantafyllidis, 2016). Such modelling can also be used to evaluate how changes in pH, temperature and solution composition affect the thermodynamic state of individual mineral phases and their potential interactions with the aqueous solution.

Therefore, further research is required to evaluate whether environmentally preferable organic acids can promote the selective dissolution of targeted minerals while limiting the dissolution of associated phases. In this case, investigating the effects of temperature, pH and reaction time, together with geochemical modelling, can provide a better understanding of the mechanisms controlling mineral dissolution and element release. This is particularly relevant for systems in which the target elements are hosted by or associated with specific mineral phases, as selective dissolution of the host or associated minerals may influence the efficiency of subsequent element recovery. Such an approach can contribute to the development of more selective and environmentally friendly strategies for recovering critical raw materials from secondary resources (Banerjee et al., 2022; Abbadi and Mucci, 2024).

1.5 Research approach

The research reported in this thesis is part of a broader project aimed at developing sustainable approaches for the recovery of critical elements from mine tailings. Within this wider project, the present work specifically investigates the selective dissolution of biotite from granite mine tailings using citric acid as an environmentally friendly leaching

agent. The study focuses on understanding the influence of operating conditions on mineral dissolution and the release of major and REEs into solution to develop a selective dissolution process.

The use of citric acid is one of the most effective and sufficient ways for biotite dissolution (Li et al., 2016). It works as a proton donor and a strong chelating ligand, so it enhances the dissolution of biotite either by proton-promoted reactions or by complexation (Huang et al., 2014; Li et al., 2016). The effects of citric acid on element mobility and geochemical processes are illustrated in Figure 5.

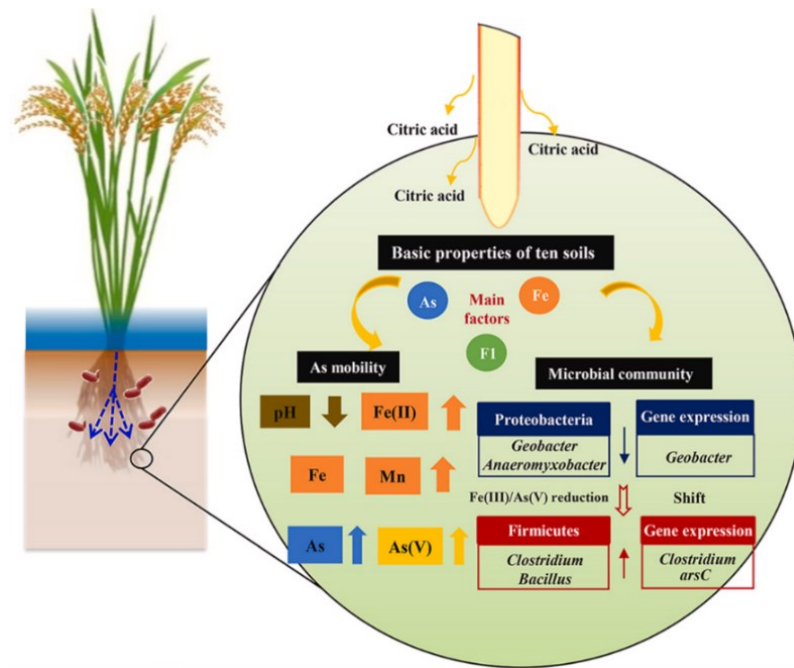


Figure 5 Schematic representation of the effects of citric acid on element mobility and geochemical processes in soil. Source: Zou et al. (2024).

During the proton-promoted dissolution, there is the release of H^+ ions from the acid, which attack the mineral surface and crystal structure weakens. Potassium ions are replaced by H^+ , Fe-O and Mg-O bonds weaken and the crystal lattice breaks. At this case, edges of the mineral dissolve faster and surface defects form. Structure becomes destabilized and Fe and Mg are released in the solution from the octahedral sheets. After that the ligand-promoted dissolution takes place. Dissolved metal ions (e.g. Fe^{2+} ,

Fe^{3+} , Mg^{2+} and Al^{3+}) could make stable complexes with citric acid ions. As a result, citrate complexation can enhance the mobility of dissolved metal ions and reduce their tendency to accumulate at the mineral surface, promoting their transfer into solution. The formation of complexes of an acid with a metal can enhance the mobility of dissolved elements and may reduce their tendency to accumulate at the mineral surface. However, secondary surface coatings may still develop depending on the solution composition and reaction conditions (Huang et al., 2014). Combination of this two mechanisms makes the citric acid more effective for biotite dissolution. Compared to the other inorganic acid, it has low toxicity, is less corrosive and biodegradable (Li et al., 2016).

To gain an insight into the process kinetics and efficiency, flow-through dissolution experiments were carried out under different temperatures and pH conditions. The concentrations of dissolved elements were determined using inductively coupled plasma mass spectrometry (ICP-MS). This allows to evaluate the mineral dissolution behaviour and extraction efficiency. In addition, geochemical modelling using PHREEQC (Parkhurst and Appelo, 2013) was performed to simulate mineral dissolution and compare the predicted concentrations with the experimental results.

The combination of laboratory experiments and geochemical modelling provides a better understanding of the dissolution kinetics of minerals under environmentally sustainable conditions. The results of this study contribute to the development of more sustainable extraction methods for recovering critical elements from mine tailings.

2 Materials and methods

2.1 Mine tailings

The material used in this study was provided by Minerali Industriali S.r.l. and consists of magnetically separated waste generated during feldspar production from granitic ore. The material comes from the Montorfano and Monte Camoscio quarries located in Piedmont, northern Italy. Previous studies have shown that these granite mine tailings are enriched in critical elements, including Ce, La, Nd, Y, Pr, Dy and Sc. The material is also characterized by the presence of Fe- and Mg-bearing silicate minerals, particularly biotite, together with accessory REE-bearing minerals such as monazite.

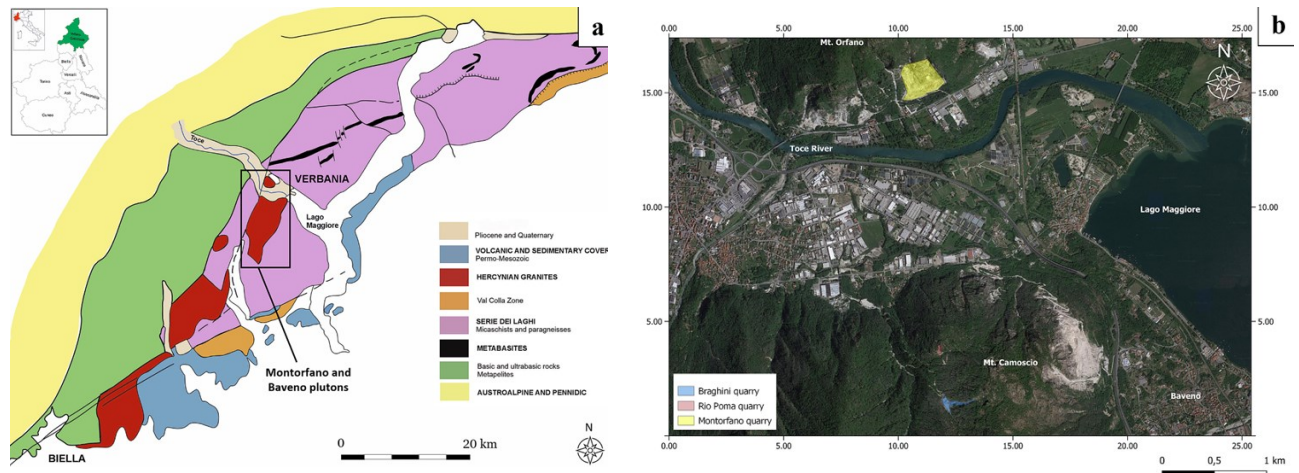


Figure 6 a) Geological map of the Lake District (Central-southern Alps) and location of Montorfano and Baveno Plutons into “Serie dei Laghi” (1:50.000 after Boriani et al., 1977); b) Location of Montorfano and Rio Poma and Braghini quarry disposal sites (Piedmont, N Italy). Source: Gioiello, S., Cazzaniga, A., Bouzahzah, H., Pirard, E., & Santoro, L. (2025). Re-use of Montorfano granite waste (Verbania, Piedmont, Italy) for REEs-recovery along the feldspar industrial chain. Results from pre-concentration tests.

Granite is a coarse-grained intrusive igneous rock composed mainly of quartz, feldspars and mica minerals. Among the mica minerals, biotite is of particular interest because it is one of the main Fe- and Mg-bearing phases and is more susceptible to acid dissolution than the surrounding silicate minerals. Granite grains are predominantly coarse due to slow crystallization of silica-rich magma deep within the Earth’s crust. It is one of the

most abundant continental crust rock because of its mineralogical stability and high silica-rich content. Granites represent a source of critical raw minerals, which can host REEs (USGS, 2025).

Four samples were used (0 - 100 μm , 100 - 300 μm , 300 - 600 μm , 100 - 600 μm), and three of them were magnetically separated (100 - 300 μm , 300 - 600 μm , 100 - 600 μm).

The fraction of SNG 100 - 300 μm was used for further analysis, and dissolution and leaching tests, because of its lower heterogeneity.

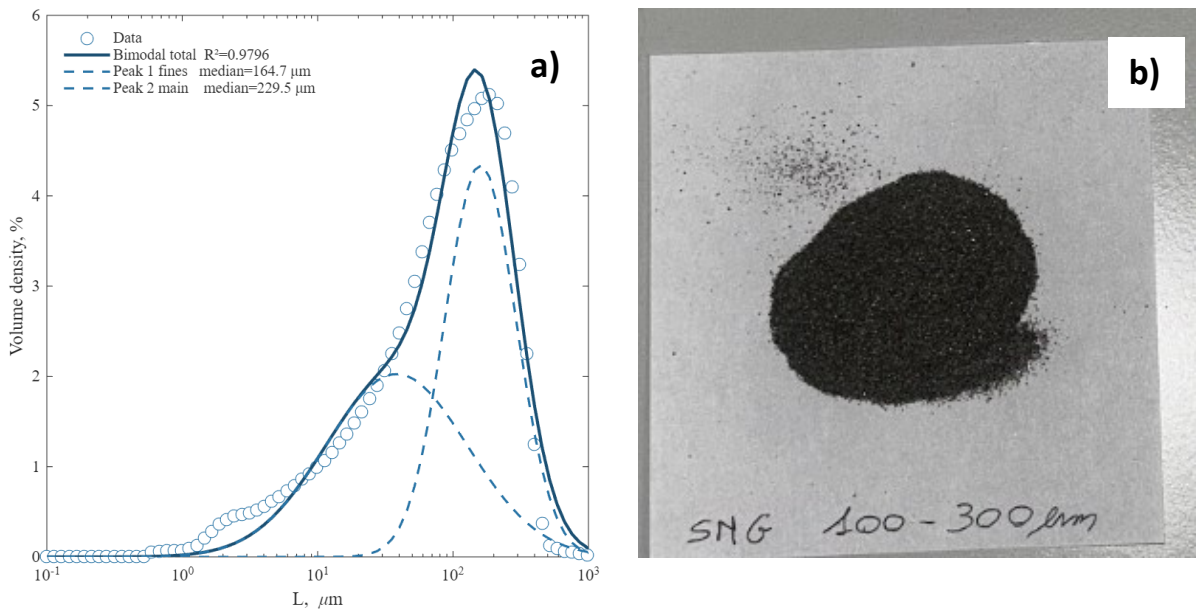


Figure 7 a) Particle-size distribution of the 100–300 μm granite mine-tailings fraction. b) Photograph of the SNG 100–300 μm fraction used for further analysis and dissolution experiments.

2.2 Material characterization

X-ray fluorescence (XRF) analysis was performed to determine the elemental composition of the sample using X-Ray Fluorescence Panalytical Zetium WDS sequential spectrometer. The results obtained from the XRF analysis were used as input for the calculations supporting the dissolution experiments.

X-ray diffraction (XRD) analysis was done to obtain the accurate mineralogical composition of the sample using PANalytical X'Pert Pro MPD diffractometer equipped with an X'Celerator detector.

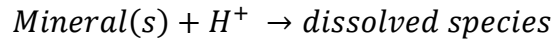
Understanding the distribution of elements among the mineral phases is important for interpreting the dissolution behaviour of the sample. REEs are mainly associated with monazite, while Fe, Mg, and K are predominantly associated with biotite. Si and Al are mainly hosted by quartz and feldspars, while chlorite also contains Fe and Mg (Rasool, 2025; Watts and Fisher, 2021). Therefore, identifying the mineral hosts of the elements is important for interpreting the leaching results and evaluating the selectivity of the dissolution process. In this study, the aim is to promote the dissolution of biotite while limiting the dissolution of the REE-bearing monazite.

2.3 Geochemical modelling

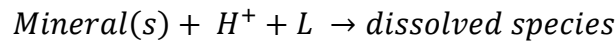
2.3.1 Mineral dissolution rates calculations

Mineral dissolution-rate calculations were performed to evaluate the expected dissolution behaviour of target mineral phases under the acidic conditions investigated in the laboratory experiments. The calculations were performed as part of a collaboration with the supervisors' research activities and were based on the inversion of the population balance equation (PBE) model over measurement taken during the experiments. Biotite and Fe-chlorite were selected as the principal target minerals because of their presence abundance in the investigated granite tailings. Monazite and bastnaesite were the REE-bearing minerals with the latter the more soluble under the experimental conditions applied. Monazite was used as a literature-based comparative reference for the experimental dissolution behaviour of bastnaesite, as both minerals represent REE-bearing phases identified in the investigated material.

Mineral dissolution can be schematically represented as a proton-promoted surface reaction, in which hydrogen ions interact with the mineral surface and promote the release of dissolved components:



In the presence of an organic ligand, the released components may additionally interact with the ligand in solution. Therefore, the general dissolution process can be represented as a proton- and ligand-promoted reaction:



where L represents the ligand present in solution. The specific contribution of the ligand depends on the mineral and on the rate formulation adopted from the corresponding literature study.

The mineral dissolution-rate equation follows the Arrhenius's equation and accounts for hydrogen ion activity, temperature, and the activation energy of the dissolution reaction:

$$r = \sum_i A_i a_{H^+}^{n_i} a_L^m e^{\frac{-E_{a,i}}{RT}} \left(1 - \exp\left(-\frac{A}{\sigma RT}\right) \right) \quad (1)$$

where r is the mineral dissolution rate, A_i is the pre-exponential factor, a_{H^+} is the activity of hydrogen ions, a_L is the activity of the ligand (i.e., the organic ion affecting the dissolution), n_i is the reaction order with respect to hydrogen-ion activity, $E_{a,i}$ is the activation energy, R is the gas constant, T is the absolute temperature, A is the chemical affinity of the dissolution reaction, and σ is Temkin's average stoichiometric number (Heřmanská et al., 2022).

Under the strongly acidic, far-from-equilibrium conditions investigated in this study, chemical affinity effects are negligible (the affinity term approaches unity) and the activity of the ligand is negligible. Consequently, the rate expressions were simplified according to the formulations and assumptions associated with the individual mineral kinetic datasets. The literature parameters were applied to evaluate the dependence of dissolution rate on hydrogen-ion activity and temperature.

For biotite, the kinetic parameters reported by Heřmanská et al. (2022) were used. The corresponding rate expression accounts for the dependence of dissolution on hydrogen-ion activity and temperature. The temperature dependence of the kinetic parameters was described using the Arrhenius relationship:

$$A(T_2) = A_0 \exp \left[-\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right] \quad (2)$$

For chlorite, an acid-catalysed dissolution-rate expression derived by Smith et al. (2013) from high-temperature mixed-flow reactor experiments was used:

$$r = k_{acid,298} \exp \left[-\frac{E_{acid}}{R} \left(\frac{1}{T} - \frac{1}{298.15K} \right) \right] a_{H^+}^n \quad (3)$$

where $k_{acid,298}$ is the acid dissolution-rate constant at 25 °C, E_{acid} is the activation energy, and n is the reaction order with respect to hydrogen-ion activity.

For the REE-bearing phases, dissolution rates were calculated using the kinetic parameters reported by Oelkers and Addassi (2025). Their database provides experimentally constrained dissolution-rate parameters for non-silicate minerals, including phosphate and carbonate minerals. The corresponding literature formulations were used to estimate the dissolution behaviour of the REE-bearing phases under the investigated acidic conditions.

The literature-derived dissolution rates were evaluated over a pH range of 1.0 - 6.0 and at temperatures between 25 and 120 °C. This range was selected to cover the acidic conditions relevant to the experiments and to evaluate the effect of temperature on the predicted mineral dissolution behaviour. The calculated rates were normalized to unit surface area and expressed as $\log_{10}(r)$ with r in $\text{mol cm}^{-2} \text{s}^{-1}$.

For each mineral phase, dissolution-rate curves were calculated as a function of pH at several temperatures within the 25-120 °C range. This allowed the effects of both pH and temperature on the predicted dissolution rates to be assessed. The calculated curves were subsequently compared with the experimental dissolution-rate values obtained in this work. In particular, the 100 °C predictions were used for comparison with the experimental results presented in Section 3.2.

2.3.2 Mineral saturation indexes

Geochemical modelling was performed using PHREEQC Version 3 (Parkhurst and Appelo, 2013) to evaluate mineral–solution interactions under the conditions selected for the dissolution experiments. PHREEQC is a geochemical modelling program that can be used for aqueous speciation, mineral saturation-index calculations, reaction-path calculations and one-dimensional transport modelling (Parkhurst and Appelo, 2013). In this study, the modelling was used to provide a thermodynamic assessment of the behavior of the mineral phases present in the initial sample and to support the interpretation of the subsequent dissolution experiments.

The simulations were conducted using the experimental material and solution compositions as input conditions. A solid-to-liquid ratio corresponding to 1 g of SNG 100-300 material in 500 mL of solution was considered. The model temperature was set to 100 °C, corresponding to the experimental temperature. The simulations were carried out considering the atmospheric pressure. Two solution conditions were investigated, with initial pH values of 2 and 3, respectively. In both cases, citric acid at 0.1 mol kg⁻¹ was considered as the leaching solution. For the pH 3 condition, 0.06 mol kg⁻¹ NaOH was included to reproduce the solution composition used in the corresponding experiment.

The calculations were used to determine the saturation index (SI) of the potentially forming mineral phases upon complete dissolution of the mine tailings. The SI is defined as the logarithm of the ratio between the ion activity product (IAP) and the equilibrium constant (K) of the corresponding mineral phase (Parkhurst and Appelo, 1999).

$$SI = \log \left(\frac{IAP}{K_{sp}} \right) \quad (4)$$

PHREEQC simulations were performed to evaluate the saturation state of minerals under the selected experimental conditions. The SI was used to determine whether the solution was undersaturated, saturated or supersaturated with respect to individual mineral phases. An SI value greater than 0 indicates supersaturation, meaning that

precipitation of the corresponding mineral is thermodynamically possible. An SI value equal to 0 indicates saturation and equilibrium between the mineral and the solution, while an SI value lower than 0 indicates undersaturation, for which precipitation is not expected.

The calculated saturation indices were subsequently processed and visualized using MATLAB (MathWorks, 2026). The results obtained from the geochemical modelling are presented and discussed in Section 3.2.2.

2.3.3 Stoichiometric relationships between released elements

Stoichiometric calculations were performed to further assess the mineral phases potentially contributing to elemental release during Experiments 1 and 2. The calculations were carried out within the broader research activities of the supervisors and were based on the theoretical elemental proportions of selected mineral phases identified in the investigated granite tailings.

The relationships between selected pairs of elements were evaluated based on the theoretical molar ratios of the corresponding elements in the considered mineral phases. For the REE-bearing minerals, the relationships between La-Ce and Nd-Ce were evaluated for monazite, bastnaesite, and allanite. For the Fe- and Mg-bearing silicate phases, the relationships between Fe-Al and Mg-Al were evaluated for biotite and chlorite.

The theoretical relationships between two elements i and j were expressed using the general stoichiometric relationship:

$$m_j = r_{j-i} \cdot m_i$$

where m_i and m_j represent the amounts of elements i and j , respectively. This same relationship was applied to all selected element pairs, namely La-Ce, Nd-Ce, Fe-Al, and Mg-Al.

2.4 Dissolution experiments

2.4.1 Set-up

The set-up used for the dissolution tests was a flow-through reactor comprising an autoclave (Uniclave, Büchi, Switzerland) with a double-wall jacket glass vessel of 600 mL volume (Figure 9), of which 500 mL was occupied by a suspension during the experiments. The suspensions were continuously stirred at 600-950 rpm to avoid particle settling, and the system was monitored with temperature and pH probes.

A double-head peristaltic pump (Masterflex, Fisher Scientific, Italy) was used to supply and withdraw a solution of given composition at 0.5 mL min^{-1} .

Liquid samples were taken from the effluent at regular intervals (10 minutes) using a fraction collector (FC204, Gilson, Italy) and analyzed as described in the ICP-MS section below.

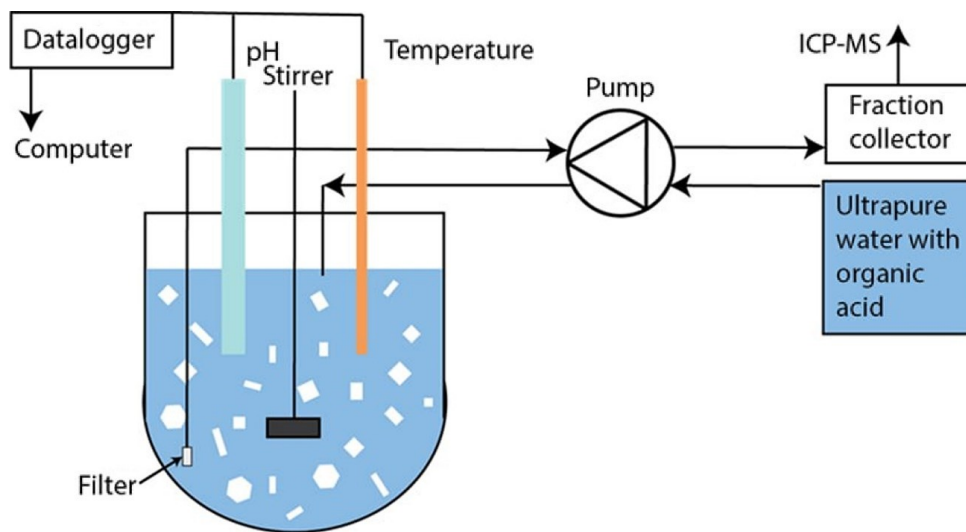


Figure 8 Schematic representation of the flow-through reactor used for the dissolution experiment



Figure 9 Photograph of the experimental set-up used for the dissolution experiments

2.4.2 Experiments

Two experiments were run at 100 °C under atmospheric pressure. Solutions of ultrapure water with a resistivity of 18.2 MΩ cm (Milli-Q, Millipore, Merck) and citric acid (Merck, Italy) were prepared. A concentration of 0.1 mol kg⁻¹ was used for the acid. Such high concentrations provide not only a large amount of leaching agents but also help regulate the pH of the solution, reaching values as low as 2.5 for 0.1 M of organic acid used.

Initially, approximately 1 g of mine tailings was placed in the reactor vessel and heated to the desired temperature, while the solution was supplied using the peristaltic pump. The initial solution was added to reach a total volume of 500 mL. After the initial filling and heating stage, the experiments were started and continued for approximately 24 h. During the experiments, the solution was continuously supplied at a flow rate of 0,5 mL min⁻¹, while the suspension was stirred at 600 rpm to avoid particle settling, and the system was monitored with temperature and pH probes.

In Experiment 1, 0.997 g of SNG 100-300 μm material was used. The initial pH of the injected solution was 2, and no NaOH or HCl was added. The experiment was conducted at 100 °C for 24 h.

In Experiment 2, 1.002 g of SNG 100-300 μm material was used. The initial pH of the injected solution was 3, obtained by adding 0.06 mol kg^{-1} NaOH. The experiment was conducted under the same conditions as Experiment 1, at 100 $^{\circ}\text{C}$ for 24 h.

Liquid samples were taken from the effluent at regular intervals (10 minutes) using a fraction collector (FC204, Gilson, Italy) and analyzed as described in the ICP-MS section below. The experimental conditions applied are listed in Table 1.

Table 1 Experimental conditions of the dissolution experiments

Parameter	Experiment 1	Experiment 2
Material	SNG 100-300 μm	SNG 100-300 μm
Mass (g)	0.997	1.002
Initial pH	2	3
Citric acid (mol kg^{-1})	0.10	0.10
NaOH (mol kg^{-1})	-	0.06
Temperature ($^{\circ}\text{C}$)	100	100
Solution volume (mL)	500	500
Flow rate (mL min^{-1})	0.5	0.5
Stirring rate (rpm)	600	600
Duration (h)	24	24

2.5 ICP-MS analyses

The concentration of the elements of interest in the liquid samples was determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Samples were diluted at 1:10 or 1:100 with a 2% HNO_3 solution. The trace element analyses were performed with an Agilent 8900 triple quadrupole inductively coupled plasma mass spectrometer (ICP-QQQ) using Rh and Re as internal standards (Labking internal standard 1000 mg L^{-1}). Multi-standard solutions of the elements of interest were prepared by adequately diluting the ICP standard solutions (Labking 33 elements 100 mg L^{-1} and 4 elements 1000 mg L^{-1}) and acidifying them with HNO_3 to a final 2% HNO_3 concentration. Accuracy and precision, calculated based on repeated sample analyses, certified reference material (NIST 1643), and in-house reference material, were better than 10% for all the analyzed elements.

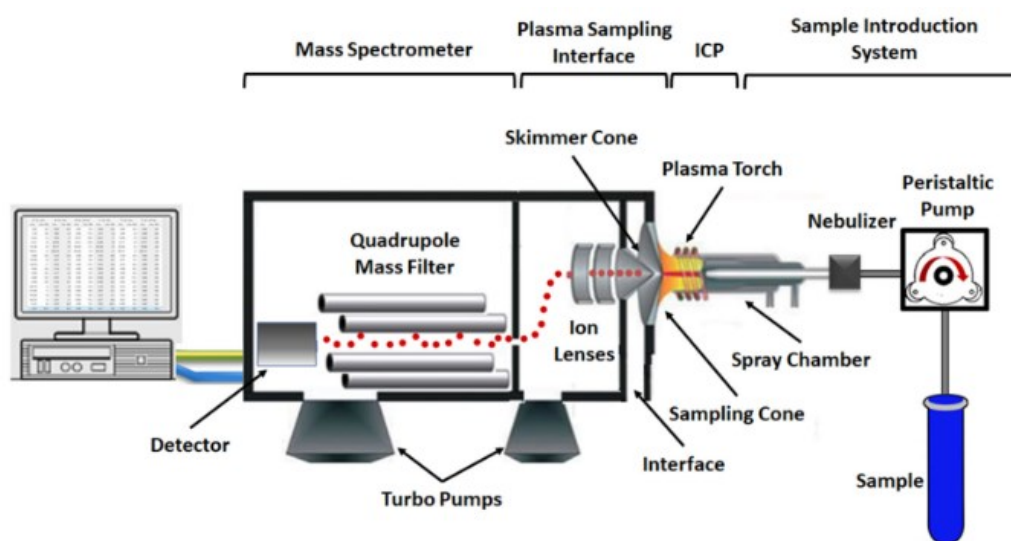


Figure 10 Schematic diagram of the main components of the ICP-MS. Source: Mazarakioti et al., 2022.



Figure 11 ICP-MS instrument used for the analysis of liquid samples at the Department of Geosciences, University of Padova.

3 Experimental results and analysis

3.1 Material characterization

The XRF analysis showed that the major element composition of the SNG 100-300 μm fraction is dominated by Si, Fe, and Al, reported as oxide weight percentages (wt.% oxides). These results are consistent with the chemical composition of granite-derived materials. Based on the major element composition, a normative mineralogical calculation was also performed, which indicated that the sample is mainly composed of biotite, chlorite, and feldspars.

The XRD analysis further identified several mineral phases in the sample, including biotite, chlorite, feldspars, quartz, and monazite. The results from the XRF and XRD provided a better understanding of the chemical and mineralogical composition of the material.

Biotite is an important Fe- and Mg-bearing mica mineral and is therefore a major source of Fe, Mg, and K in the sample. Its layered structure makes it relatively susceptible to dissolution under acidic conditions, which is relevant to the carried out experiments

(Malmström and Banwart, 1997; Li et al., 2016). Monazite was identified as the primary target mineral, predominantly locked within Fe-rich biotite (Gioiello et al., 2025). It is an accessory phosphate mineral and an important host of REEs, particularly La, Ce, and Nd. Due to its stable phosphate structure, monazite is generally more resistant to dissolution than many silicate minerals. Although its dissolution increased under acidic conditions and in the presence of complexing agents (Ni et al., 2011).

The identification of biotite and monazite was particularly important for the present study. Biotite is the main target mineral for dissolution, while monazite represents an important REE-bearing phase that should preferably remain stable during the treatment. Therefore, the XRF and XRD results provided the basis for evaluating the selectivity of the dissolution experiments. Full atomic composition is presented in a Figure 12 in an order of the decreasing abundance.

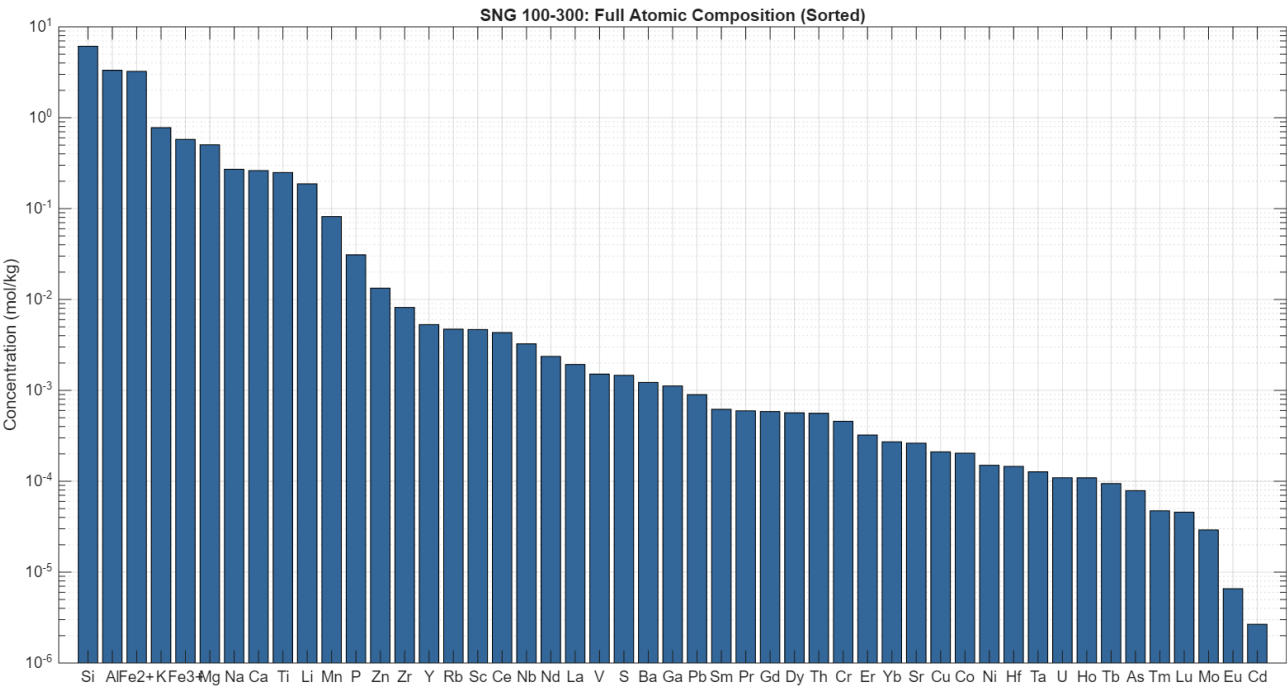


Figure 12 Elemental composition of a granite sample SNG 100-300 μm sorted by abundance

3.2 Dissolution experiments results

3.2.1 Experiment 1

The dissolution behavior of the elements released during Experiment 1 was evaluated using ICP-MS analyses of the collected solution samples. The experiment was carried out at 100°C under acidic conditions. The measured concentrations are presented in mol kgw⁻¹ as a function of reaction time (Figures 13-16). The dashed lines indicate the maximum expected concentration calculated from the initial elemental composition of the solid material, assuming complete transfer of the respective element to the aqueous phase.

Most elements showed a similar temporal trend, with concentrations increasing during the initial stage of the experiment and reaching maximum values generally between approximately 3 and 7 h, followed by a gradual decrease towards 24 h. This indicates that element release was most pronounced during the early stage of the experiment. The subsequent decrease may be related to a reduction in the dissolution rate and/or removal of dissolved species through secondary processes such as re-adsorption or precipitation.

Among the major elements, Fe, Al and Mg showed the most pronounced release. Fe reached approximately 5.3×10^{-3} mol kgw⁻¹, Al approximately 4.0×10^{-3} mol kgw⁻¹ and Mg approximately 7×10^{-4} mol kgw⁻¹. The strong release of Mg and Al is consistent with the dissolution of biotite, which contains both elements as major structural components. Ca, Ti, Li and Mn also increased during the initial stage before decreasing at longer reaction times. Most of these elements remained below their respective maximum expected concentrations, although Al and Mn reached or exceeded their theoretical values.

The trace elements showed more variable behavior. V, Co and Ni displayed clear increases during the early stage followed by gradual decreases, whereas Zn, Ba and Cu remained at relatively low concentrations compared with their maximum expected values. Pb showed a distinct temporary peak at approximately 4 h, after which its concentration rapidly decreased. This isolated peak should therefore be interpreted with caution.

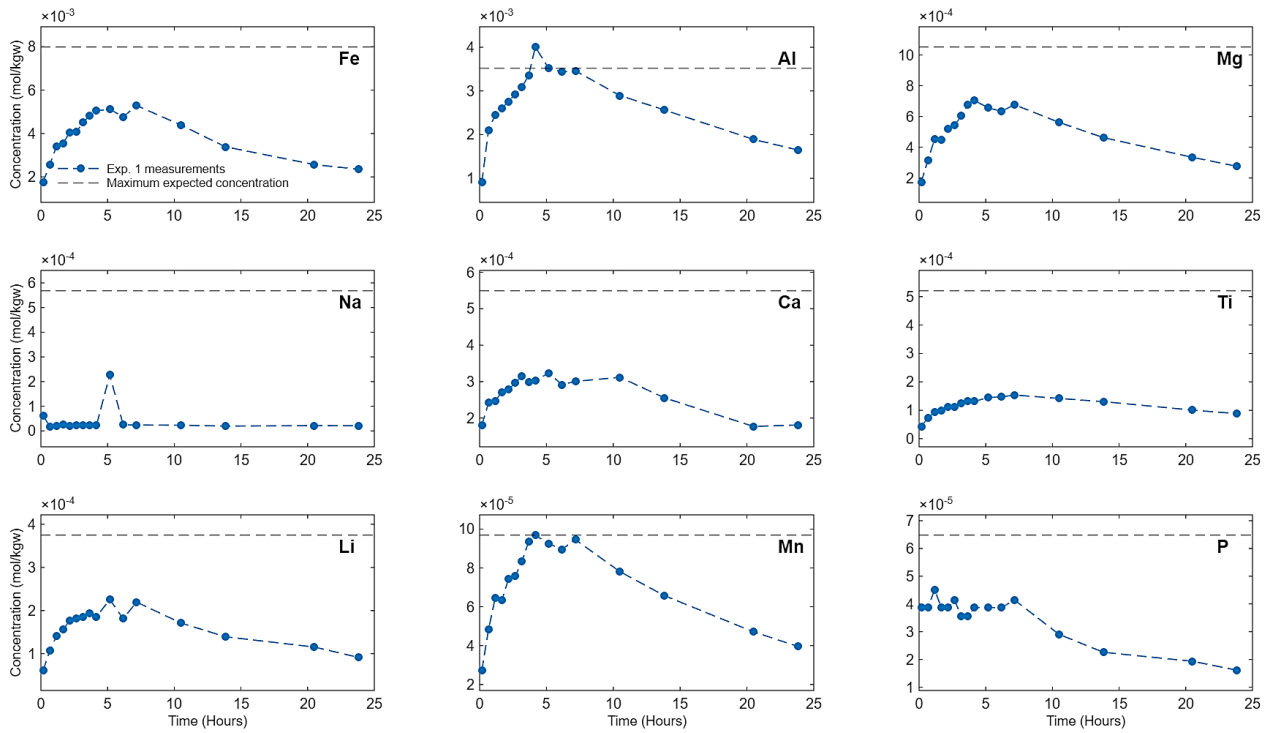


Figure 13 Temporal evolution of dissolved concentrations of major and trace elements during Experiment 1 (Group 1)

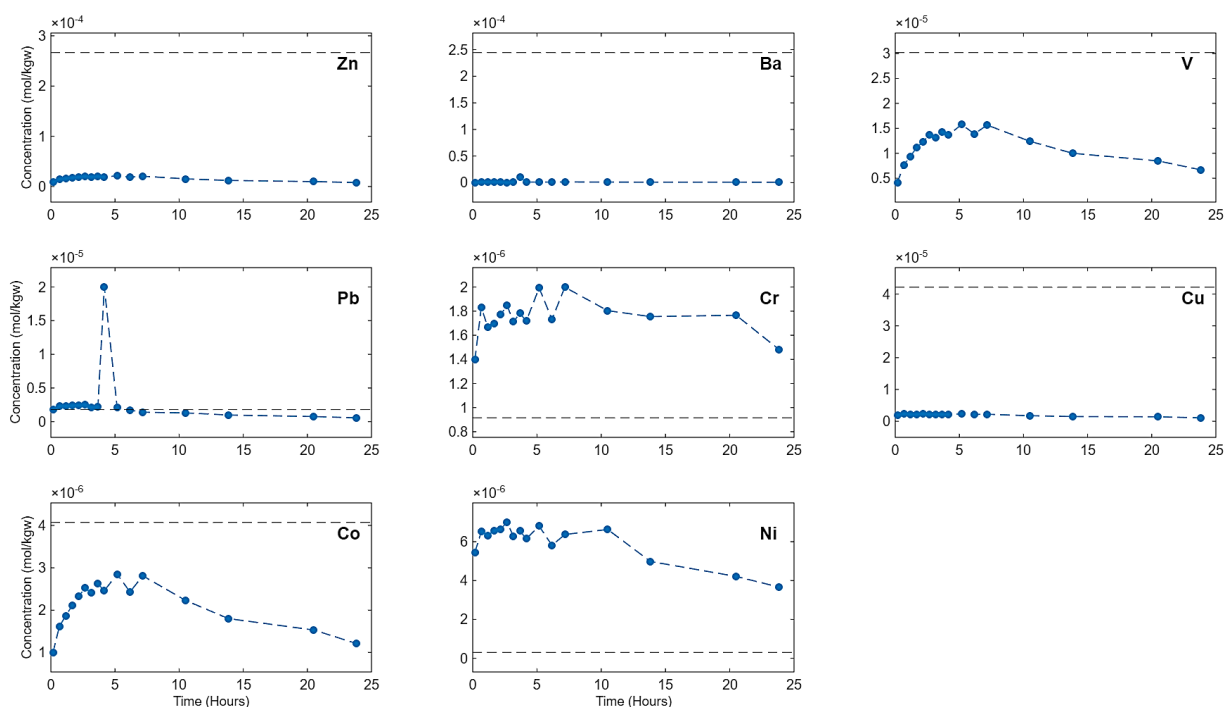


Figure 14 Temporal evolution of dissolved concentrations of major and trace elements during Experiment 1 (Group 2)

The REEs and associated elements also generally increased during the first several hours before decreasing, as shown in Figures 15 and 16. Sc, Rb, Y, La, Ce, Pr, Nd and Sm reached their highest concentrations during the early stage of the experiment. Among the REEs, Ce and Nd showed particularly pronounced concentrations, reaching approximately 180-190 ppb and 160 ppb, respectively. The heavier REEs, including Gd, Tb, Ho, Er, Tm, Yb and Lu, followed the same general pattern, although their absolute concentrations were lower. Th and U also reached maximum concentrations during the early stage and subsequently decreased.

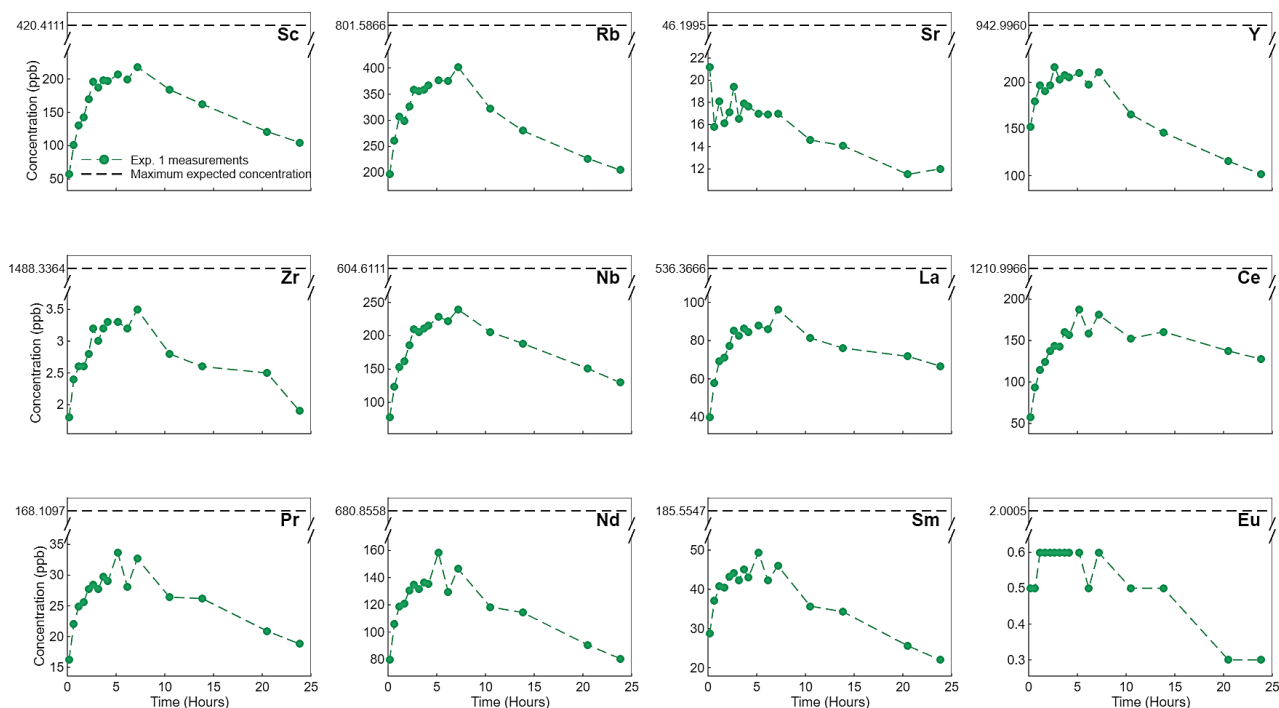


Figure 15 Temporal evolution of dissolved concentrations of REEs during Experiment 1 (Group 1)

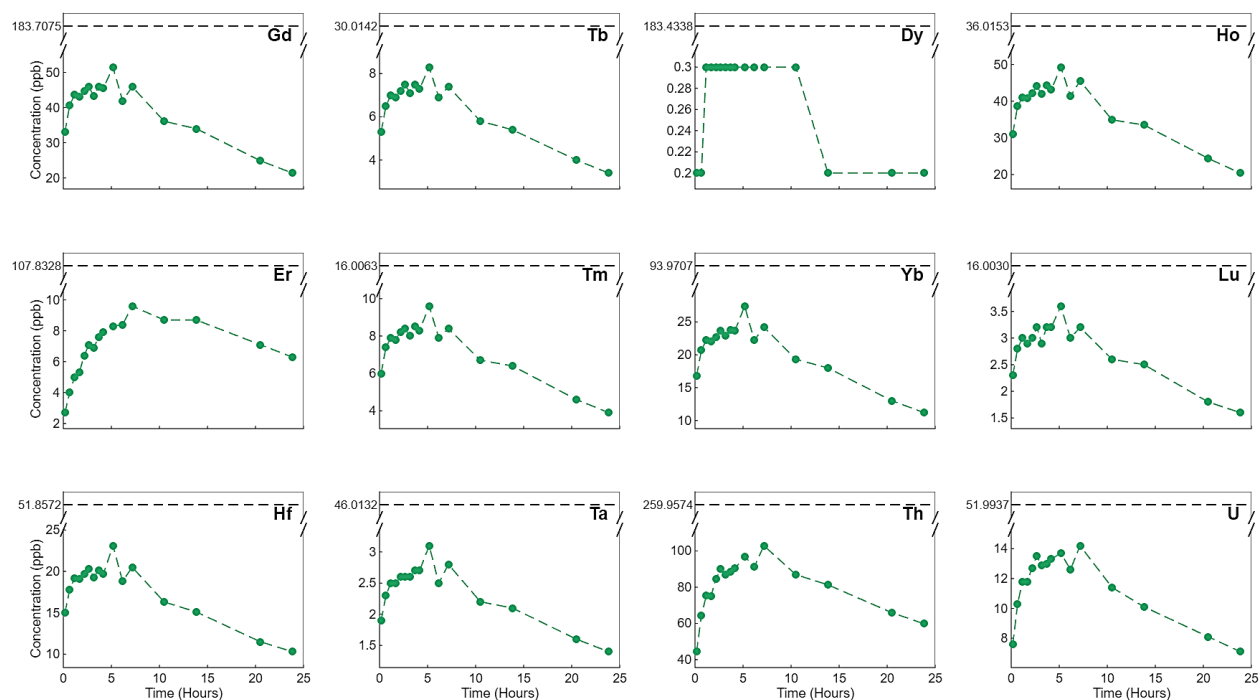


Figure 16 Temporal evolution of dissolved concentrations of REEs during Experiment 1 (Group 2)

The maximum expected concentrations provide an additional indication of the extent of element mobilization. Elements whose measured concentrations approached their theoretical maximum were released more extensively from the solid, whereas elements remaining far below this value showed more limited mobilization under the experimental conditions. However, the maximum expected concentration represents a theoretical reference rather than an experimental equilibrium concentration and therefore should not be interpreted as a precipitation or saturation limit.

To compare the relative dissolution behavior of elements with substantially different absolute concentrations, the measured concentrations were normalized to their maximum measured concentration ($C/C_{\max}$) (Figure 17). The normalized plot groups elements according to the mineral phases in which they occur: Fe and Mg are shown as representative elements of biotite. Fe, Mg, Al and Mn represent chlorite. Na and Al represent albite; Ca and P represent apatite. La, Ce, Pr, Nd, Sm, Eu, Gd, Th and U represent monazite. Y, Dy, Er, Yb and Lu represent xenotime. This normalization allows the shape and timing of the concentration profiles to be compared independently of their absolute concentration

The normalized profiles show that the elements associated with apatite, biotite, albite and chlorite generally reached high relative concentrations during the first several hours, followed by a decrease. The elements associated with monazite and xenotime also show an increase during the initial stage, indicating mobilization of REE-bearing phases under the experimental conditions. However, differences in the timing and magnitude of the normalized maxima suggest that the mineral phases did not respond identically throughout the experiment. In particular, the normalized profiles provide a useful comparison for assessing whether the dissolution behavior of biotite differed from that of the REE-bearing phases.

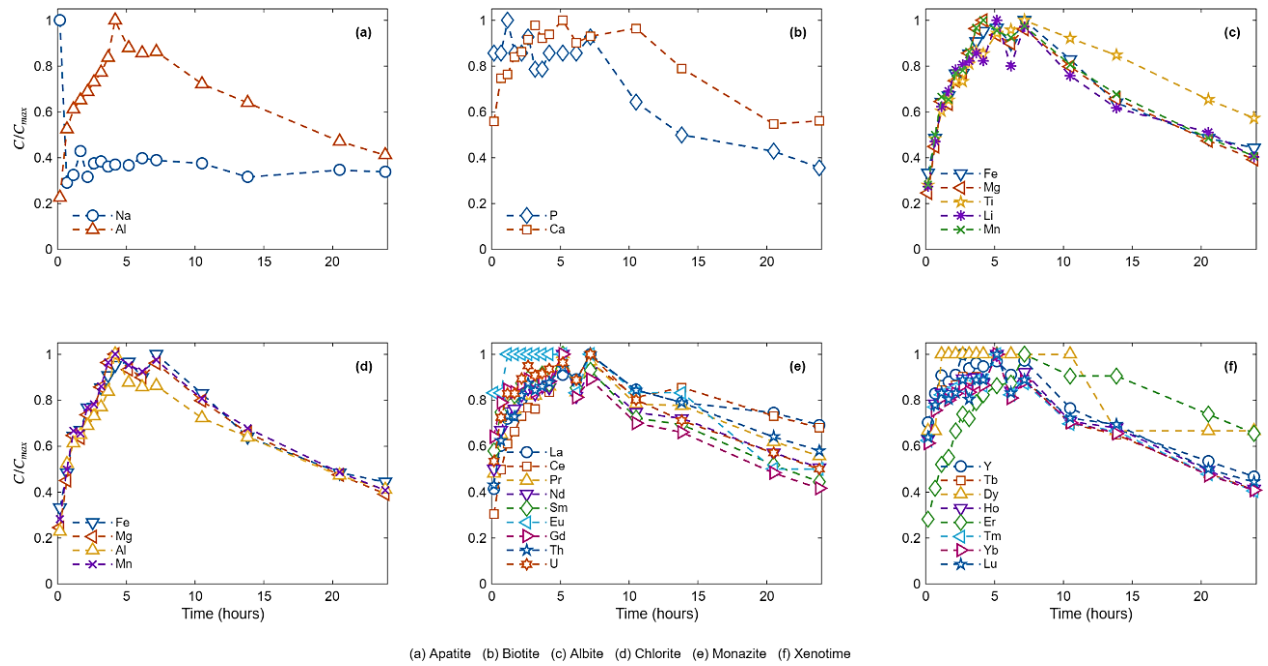


Figure 17 Normalized concentration profiles of elements associated with the main mineral phases during Experiment 1

Overall, Experiment 1 demonstrated that the dissolution process was most active during the initial hours of the experiment, when most elements reached their highest dissolved concentrations. The pronounced release of Mg and Al indicates significant dissolution of the biotite-bearing material, while the simultaneous mobilization of REEs suggests that the REE-bearing phases were also affected by the acidic conditions. However, the different concentration profiles and the varying proportions of the measured concentrations relative to the maximum expected values indicate that the elements were not released to the same extent. The normalized concentration profiles further highlight differences in the dissolution behavior of elements associated with biotite and the REE-bearing phases. These results provide the basis for assessing the selectivity and extraction efficiency of the dissolution process in the following sections.

3.2.2 Experiment 2

The dissolution behavior of the elements released during Experiment 2 was evaluated using ICP-MS analyses of the collected solution samples. The measured concentrations are presented as a function of reaction time in Figures 18-21. The dashed lines represent the maximum expected concentration calculated from the initial elemental composition of the solid, assuming complete transfer of the respective element into solution.

Most elements showed the highest degree of mobilisation during the first several hours of the experiment, followed by a gradual decrease in concentration towards the end of the experiment. Fe reached a maximum concentration of approximately $4.1 \times 10^{-3} \text{ mol kgw}^{-1}$, while Al and Mg reached approximately 3.2×10^{-3} and $5.8 \times 10^{-4} \text{ mol kgw}^{-1}$, respectively. Li and Mn also increased during the initial stage, reaching approximately 2.4×10^{-4} and $7.5 \times 10^{-5} \text{ mol kgw}^{-1}$. These concentration profiles indicate pronounced mobilisation of elements associated with the dissolution of the biotite-bearing material.

Ca showed a distinct behaviour compared with the other major elements, with a pronounced temporary peak of approximately $1.8 \times 10^{-2} \text{ mol kgw}^{-1}$ at the beginning of the experiment, followed by a rapid decrease to concentrations close to zero. In contrast, Ti remained at very low concentrations throughout the experiment, while Na was essentially absent from the solution. P increased during the initial stage and reached approximately $3.5 \times 10^{-5} \text{ mol kgw}^{-1}$ before decreasing towards the end of the experiment.

The trace elements generally occurred at lower concentrations and showed different temporal behaviours. Pb and Ni displayed relatively high initial concentrations followed by a gradual decrease, while Cr showed a distinct peak at approximately 6 h. Ba exhibited a temporary increase at around 14 h, whereas V, Cu and Co remained at relatively low concentrations throughout the experiment. Zn also remained well below its maximum expected concentration.

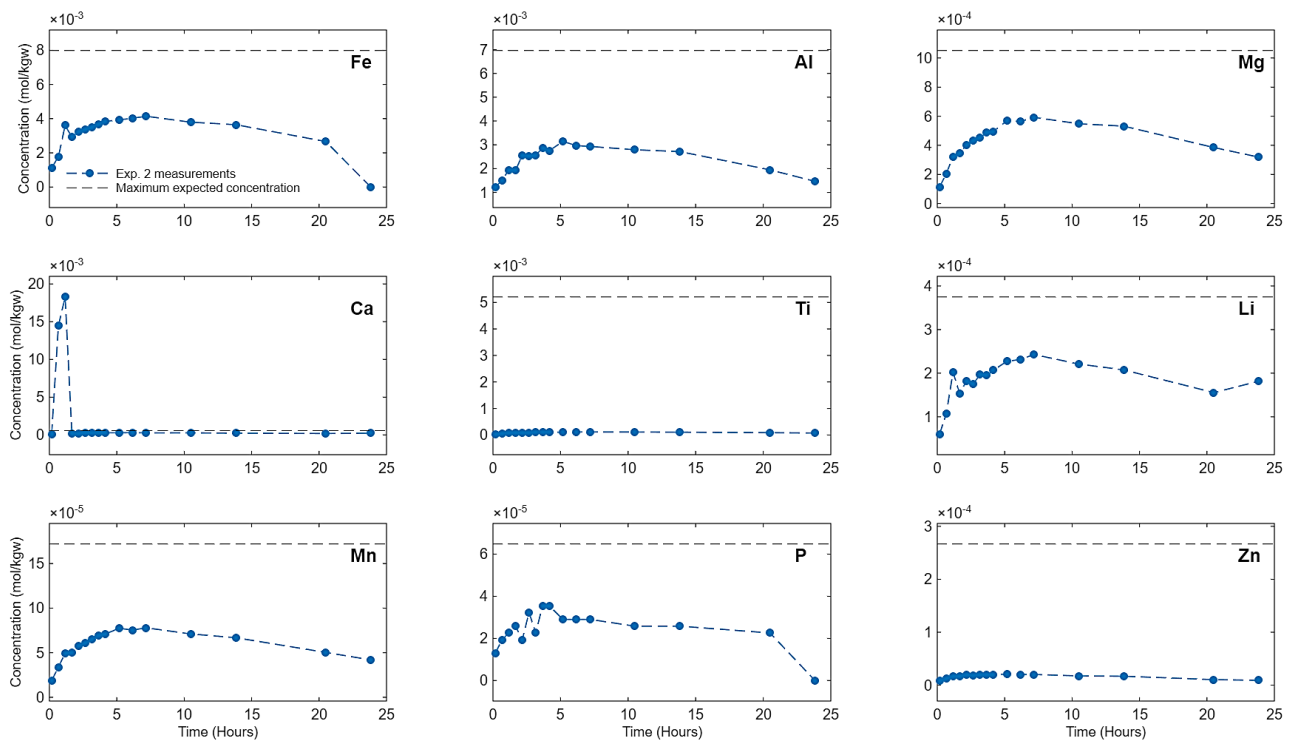


Figure 18 Temporal evolution of dissolved concentrations of major and trace elements during Experiment 2 (Group 1)

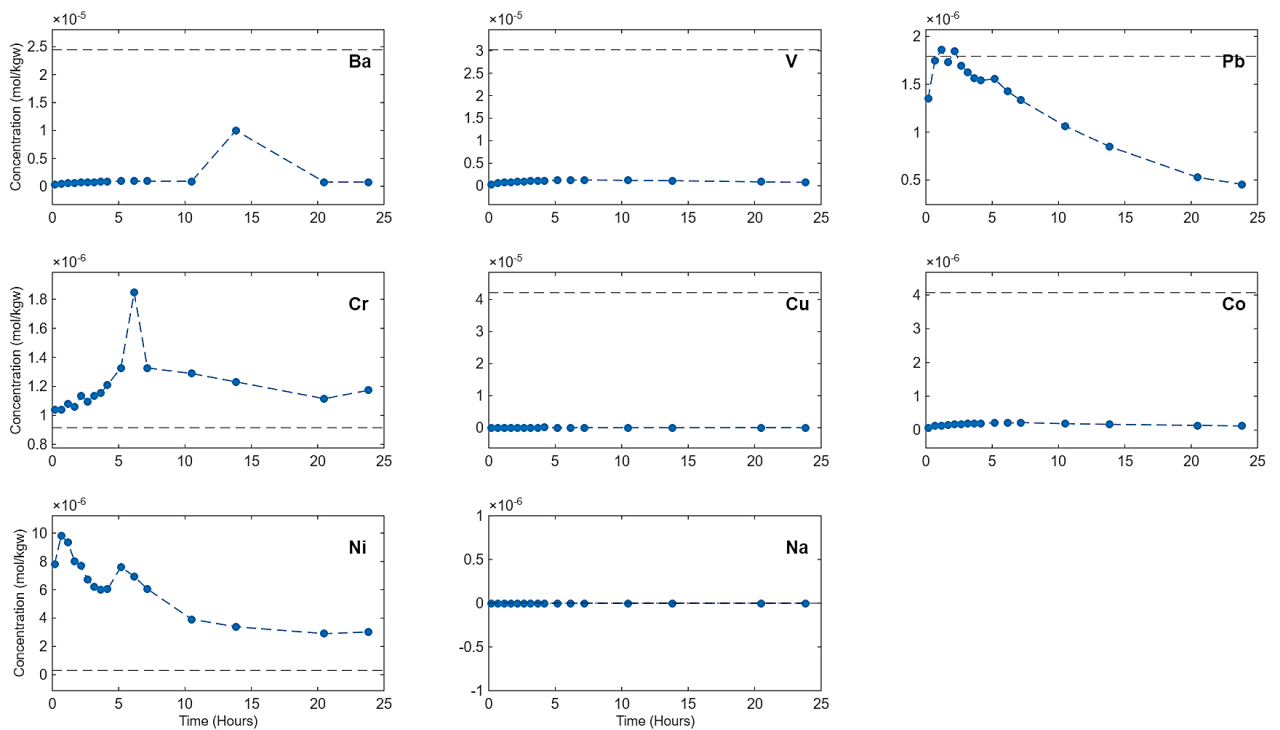


Figure 19 Temporal evolution of dissolved concentrations of major and trace elements during Experiment 2 (Group 2)

The REEs generally showed a similar pattern, with concentrations increasing during the first several hours and subsequently decreasing. Sc, Rb, Y, Zr, Nb, La, Ce, Pr, Nd and Sm reached their maximum concentrations approximately between 4 and 7 h. Among the REEs, Ce reached approximately 170 ppb, while Nd and Pr reached approximately 125 and 29 ppb, respectively. The heavier REEs, including Gd, Tb, Ho, Er, Tm, Yb and Lu, also showed clear mobilisation during the early stage, followed by a progressive decrease. Th and U followed the same general trend, reaching their maximum concentrations during the first several hours.

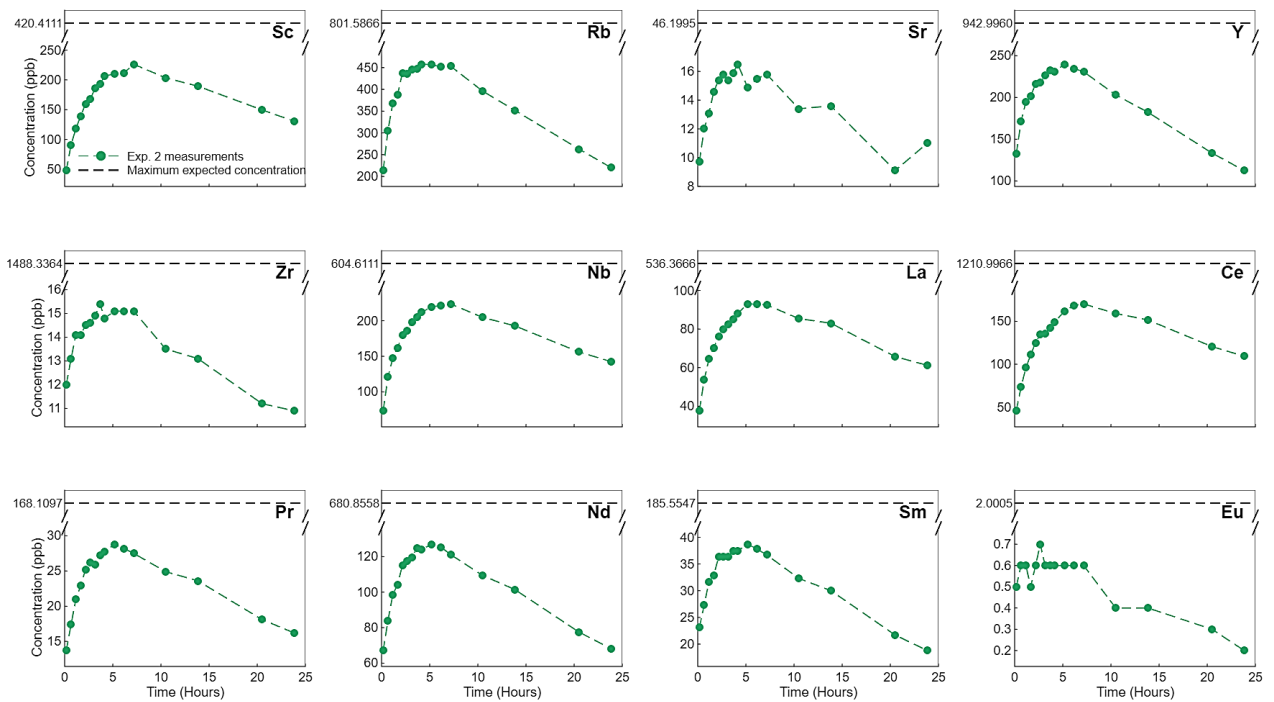


Figure 20 Temporal evolution of dissolved concentrations of REEs during Experiment 2 (Group 1)

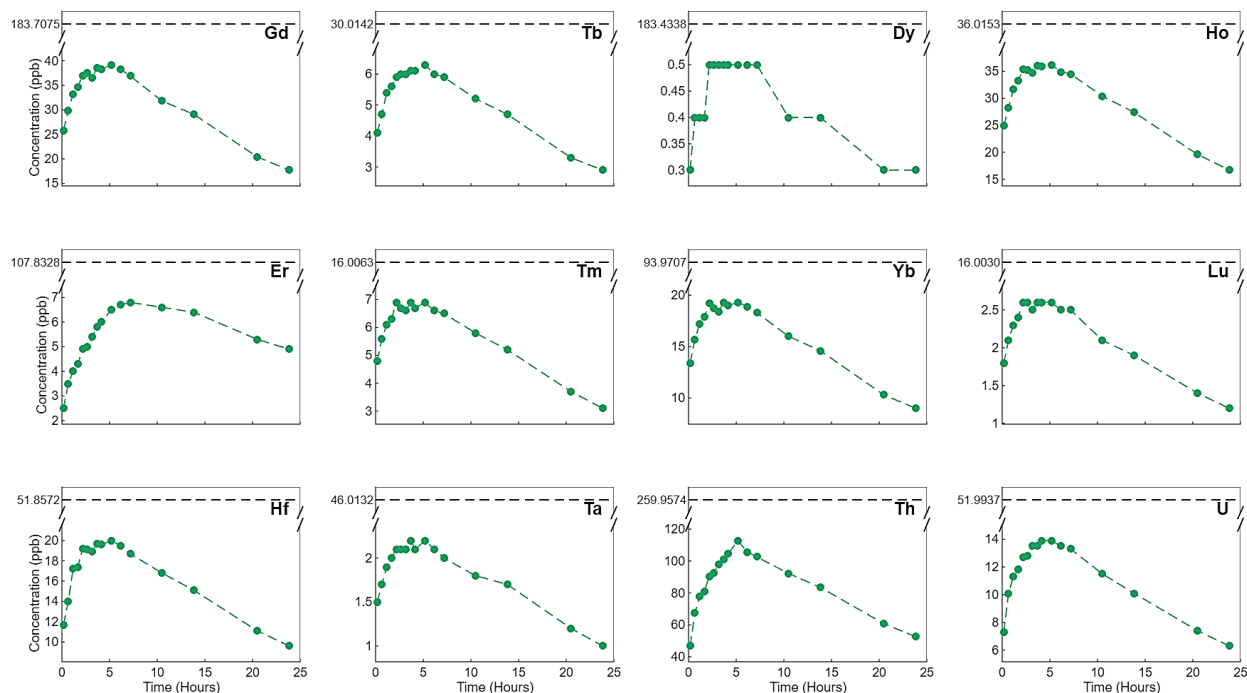


Figure 21 Temporal evolution of dissolved concentrations of REEs during Experiment 2 (Group 2)

Comparison with the maximum expected concentrations shows that most elements remained below their theoretical maximum values, indicating that complete dissolution of the corresponding elements was not achieved. The difference between the measured and maximum expected concentrations was particularly pronounced for several elements such as Ti, Zn, Cu, Co and the REEs. The maximum expected concentrations are therefore used as a reference for evaluating the relative extent of elemental mobilisation rather than as an equilibrium limit.

To compare the dissolution behaviour independently of the absolute concentrations, the measured concentrations were normalized to their maximum measured concentration ($C/C_{\max}$) (Figure 22). The normalized profiles show that elements associated with the different mineral phases generally reached their maximum relative concentrations within the first several hours. The biotite-associated elements Fe, Mg, Ti, Li and Mn show broadly similar increasing trends followed by decreasing concentrations. The elements associated with chlorite (Fe, Mg, Al and Mn) show a comparable behaviour, although their individual maxima occur at slightly different times.

The normalized profiles of the monazite-associated elements La, Ce, Pr, Nd, Sm, Eu and Gd, together with Th and U, show relatively consistent behaviour, with most reaching values close to 1 during the first 5-7 hours and subsequently decreasing. The xenotime-associated elements Y, Tb, Dy, Er, Tm, Yb and Lu also show similar profiles, although Er remains relatively high for longer compared with the other elements. The apatite-associated elements P and Ca show a markedly different behaviour, mainly because of the strong early Ca peak and the rapid decrease afterwards.

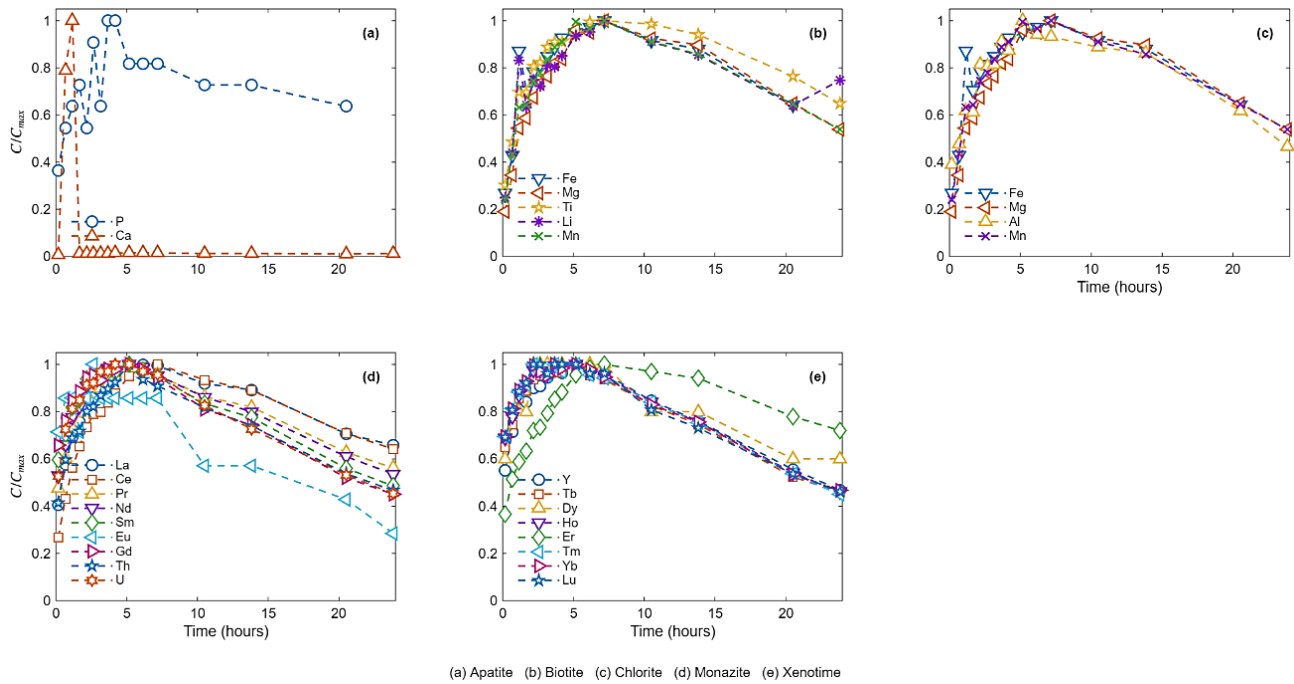


Figure 22 Normalized concentration profiles of elements associated with the main mineral phases during Experiment 2

Overall, Experiment 2 indicates that elemental mobilisation was strongest during the initial stage of dissolution. Fe, Al and Mg were the most strongly released major elements, while the REEs showed clear mobilisation from the REE-bearing phases. The normalized profiles demonstrate broadly similar temporal behaviour among several mineral-associated elements, while also highlighting differences between apatite, biotite/chlorite, monazite and xenotime. The extraction efficiency of the elements is evaluated in Section 3.3.

3.3 Efficiency of the extraction

3.3.1 Experiment 1

The extraction efficiencies obtained for Experiment 1 are presented in Figure 23. For the analyzed metals, extraction efficiencies were generally moderate, with most elements showing values between approximately 40 and 70%. Li, Mg, Mn, Cu, Zn, P, Fe and Ca reached efficiencies above 50%, indicating relatively effective mobilization under the experimental conditions. Al and V showed slightly lower efficiencies, while Ba and Na were the least efficiently extracted, with values below 10%.

The highest extraction efficiencies were observed for Cr and Ni, both exceeding the 100% reference line. Such values result from the calculated concentrations being higher than the corresponding maximum ICP-MS concentrations used as the reference and therefore should not be interpreted as more than complete extraction. The REEs generally exhibited lower extraction efficiencies than the other analyzed elements. Sc showed the highest REE extraction, at approximately 70%, followed by Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Th, which mostly ranged between 30 and 45%. La, Ce and Pr showed particularly low extraction efficiencies, while Zr and Hf were close to zero.

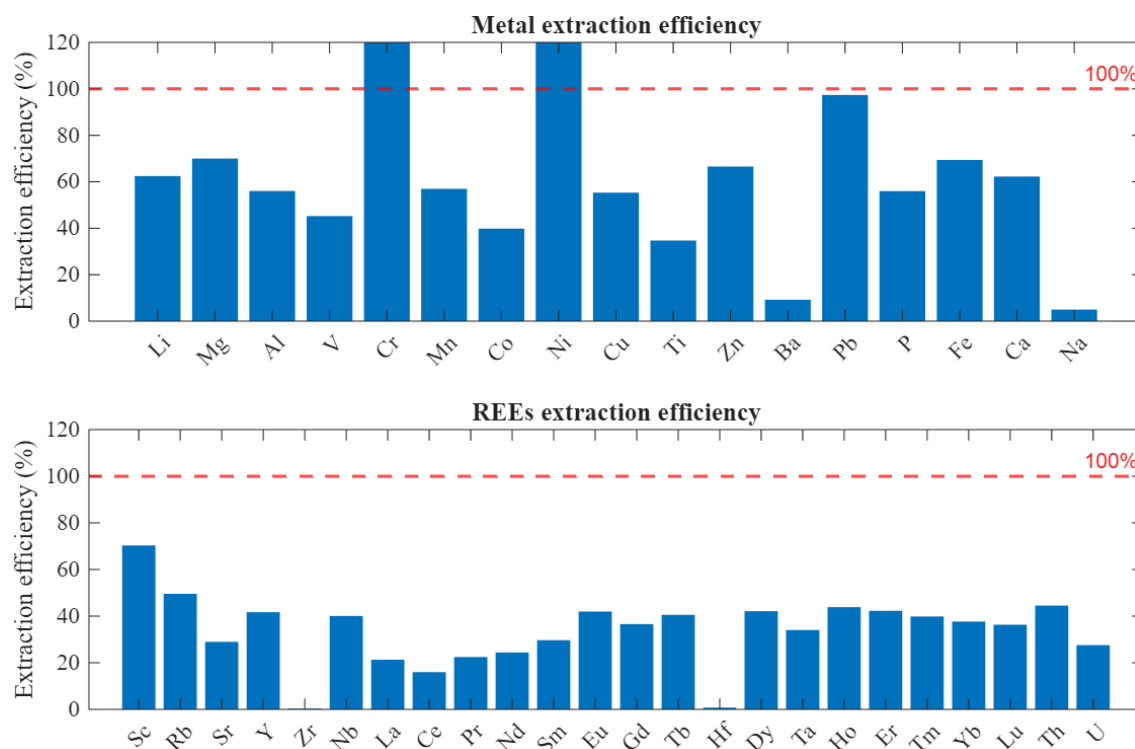


Figure 23 Extraction efficiency of major and trace elements and REEs in Experiment 1. The red dashed line represents 100% extraction efficiency.

Experiment 1 resulted in moderate extraction of several major and trace elements, whereas the extraction of most REEs remained relatively limited. This indicates that the applied experimental conditions were more effective in mobilizing some non-REE elements than the REE-bearing phases.

3.3.2 Experiment 2

The extraction efficiencies obtained for Experiment 2 are presented in Figure 24. The extraction efficiencies of the major and trace elements were generally moderate to high, with several elements showing values above 60%. Li, Mg, Zn, Pb, Fe and Ca reached extraction efficiencies between approximately 60 and 80%, indicating relatively

effective mobilization under the experimental conditions. Al, V, Mn, Co, Ti and P showed intermediate extraction efficiencies, generally between 30 and 55%. In contrast, Cu and Ba exhibited very low extraction efficiencies, below 10%.

The highest values were observed for Cr, Ni and Na, which exceeded the 100% reference line. As in Experiment 1, these values result from the measured concentrations being higher than the corresponding reference maximum concentrations and therefore should be interpreted with caution rather than as extraction above 100%.

The REEs generally showed lower extraction efficiencies compared with the major and trace elements. Sc displayed the highest extraction efficiency, at approximately 77%, followed by Rb at around 60% and Y at approximately 48%. Most of the remaining REEs showed extraction efficiencies between approximately 15 and 45%. Zr and Hf exhibited particularly low extraction, close to zero, while Ce, Pr and Lu also showed relatively low values. Among the heavier REEs, Ho, Er, Tm, Yb and Th reached moderate extraction efficiencies, generally around 30-45%.

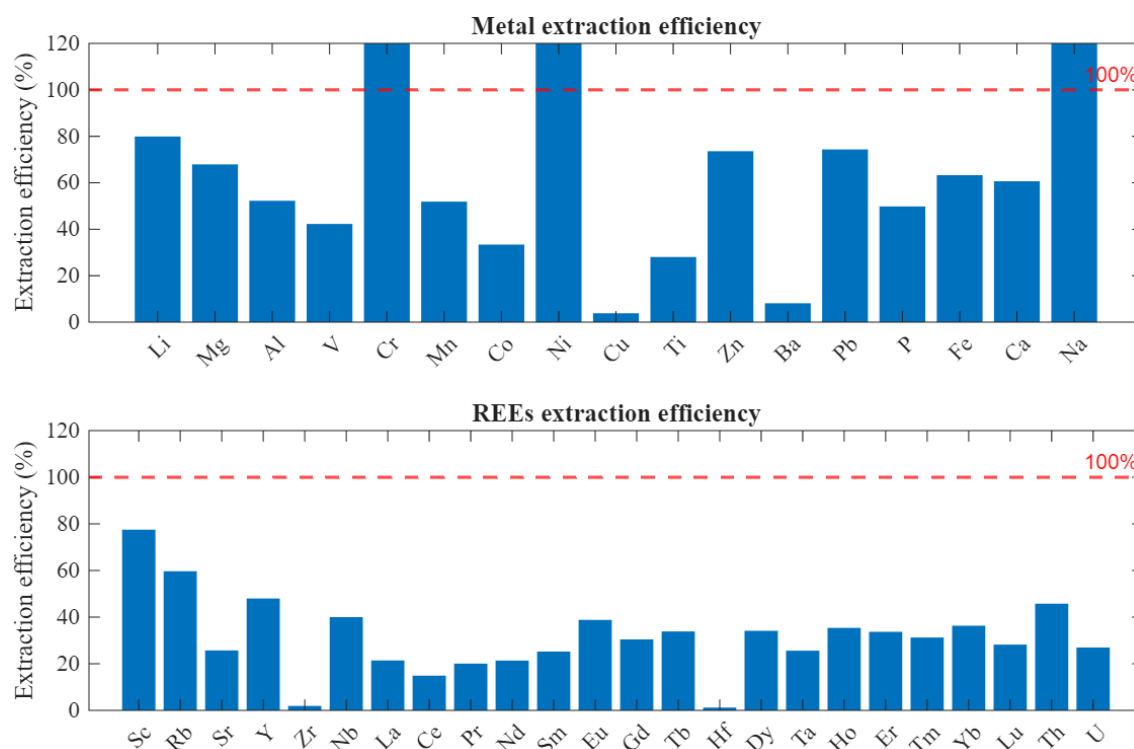


Figure 24 Extraction efficiency of major and trace elements and REEs in Experiment 2. The red dashed line represents 100% extraction efficiency.

Experiment 2 resulted in relatively efficient extraction of several major and trace elements, while the extraction of most REEs remained moderate to low. Sc, Rb and Y were the most efficiently extracted REEs, whereas Zr and Hf were poorly mobilized. This suggests that the experimental conditions promoted the dissolution and mobilization of some elements while limiting the release of several REEs.

Comparing Experiments 1(pH 2) and Experiment 2(pH 3) shows that increasing the pH from 2 to 3 had an element-dependent effect on extraction efficiency. While some elements showed lower extraction at pH 3, Li, Sc, Rb and Y showed increased extraction. Overall, the results indicate that increasing pH can modify the selectivity of element mobilization rather than simply increasing or decreasing extraction for all elements.

3.4 Geochemical modelling

3.4.1 Stoichiometric relationships between released elements

The stoichiometric relationships between the experimentally measured elements and the theoretical mineral compositions were evaluated for Experiment 1 (Figures 25 and 26). The comparison includes both REE-bearing minerals and Fe-Mg-bearing silicate minerals. The aim was to assess whether the observed elemental release was consistent with the expected mineral stoichiometry and to identify elements that can be used as indicators of mineral dissolution.

For the REE-bearing minerals (Figure 25), the La-Ce data show a clear positive relationship, with most experimental points located close to or between the theoretical relationships for monazite, bastnaesite and allanite. The Nd-Ce data also show a positive trend. However, the experimental points are generally above the theoretical relationships, indicating higher Nd relative to Ce than predicted by the idealized mineral stoichiometry.

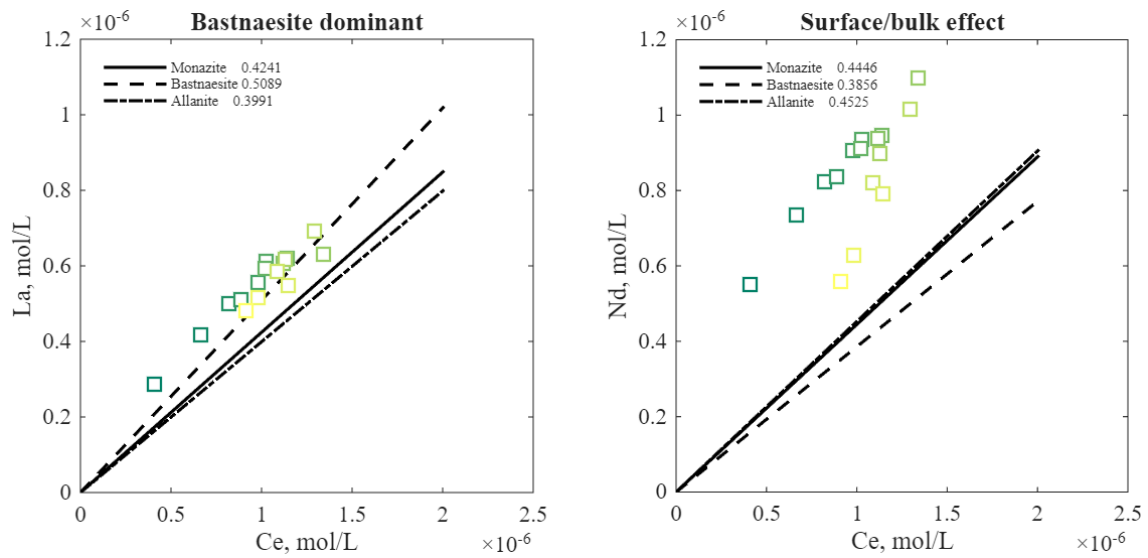


Figure 25 Stoichiometric relationships between experimentally measured and theoretical REEs concentrations for Experiment 1: La-Ce and Nd-Ce relationships for monazite, bastnaesite and allanite.

For the silicate minerals (Figure 26), the Fe-Al relationship shows a strong positive correlation, with most experimental points close to the theoretical biotite and chlorite relationships. In contrast, the Mg-Al data are generally close to the lower-slope biotite and chlorite relationships and clearly below the higher-slope chlorite relationship.

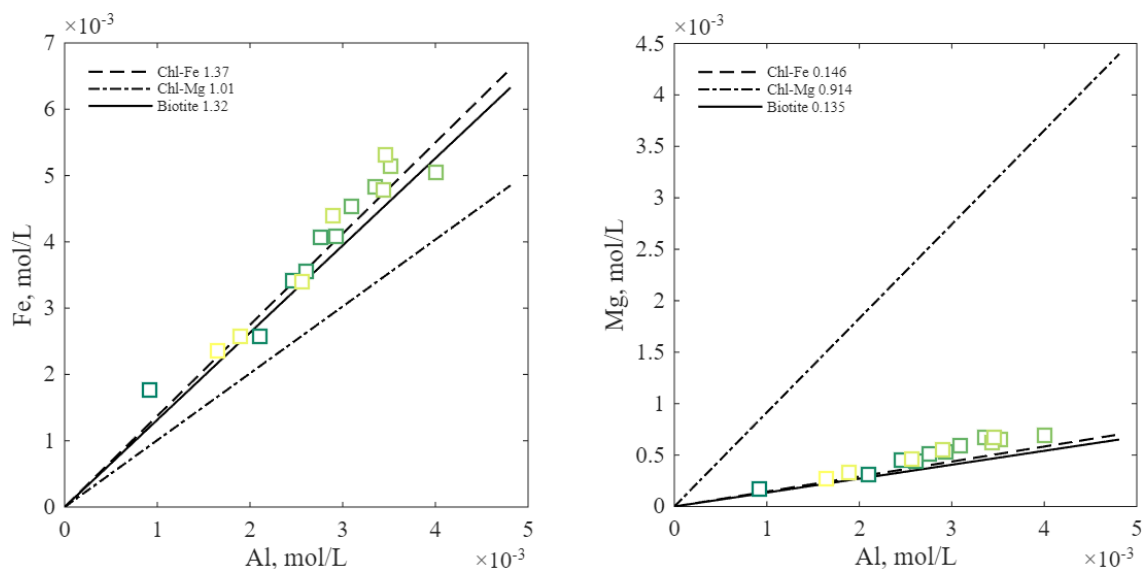


Figure 26 Stoichiometric relationships between experimentally measured and theoretical major-element concentrations for Experiment 1: Fe-Al and Mg-Al relationships for biotite and chlorite.

Generally, for Experiment 1, the stoichiometric comparison indicates that the measured elemental release is broadly consistent with the contribution of biotite and chlorite, while the REE relationships show greater deviations from the idealized compositions of the considered REE-bearing minerals. This suggests that elemental release is likely influenced by more than one mineral phase.

For Experiment 2, the stoichiometric comparison is presented in Figures 27 and 28. The comparison comprises both REE-bearing minerals and Fe-Mg-bearing silicate minerals.

For the REE-bearing minerals, the measured La concentrations are generally higher than the theoretical values calculated for monazite, bastnaesite and allanite, particularly at lower Ce concentrations. The La data points follow a relatively consistent trend and are positioned mainly above the theoretical dissolution lines. For Nd, the difference between the measured concentrations and the theoretical predictions is more pronounced, with the experimental values substantially exceeding the calculated contributions of the individual REE-bearing minerals. This suggests that the measured

REEs concentrations cannot be explained by dissolution of a single mineral phase alone and may reflect the combined contribution of several REE-bearing phases.

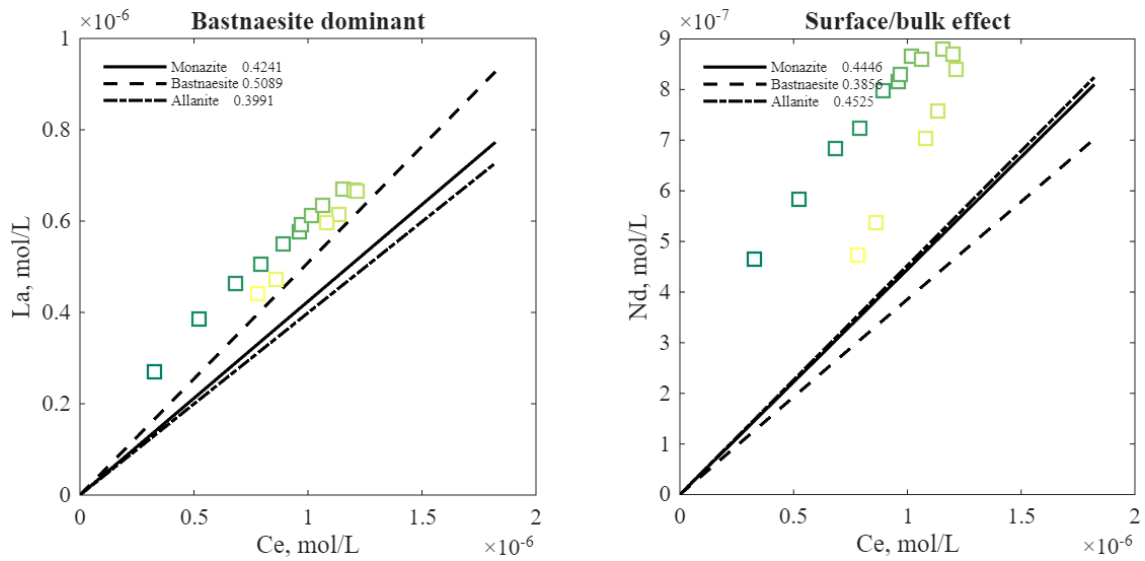


Figure 27 Stoichiometric relationships between experimentally measured and theoretical REEs concentrations for Experiment 2: La-Ce and Nd-Ce relationships for monazite, bastnaesite and allanite.

For the silicate minerals (Figure 28), the Fe concentrations show a relatively good agreement with the predicted dissolution trends of biotite and chlorite-Fe, with most experimental points located close to or between the corresponding theoretical lines. In contrast, the measured Mg concentrations remain close to the biotite and chlorite-Mg predictions, while being considerably lower than the theoretical chlorite-Mg contribution. In general, the results indicate that Fe release is broadly consistent with dissolution of biotite and chlorite, whereas the Mg data suggest a smaller contribution from chlorite under the conditions of Experiment 2.

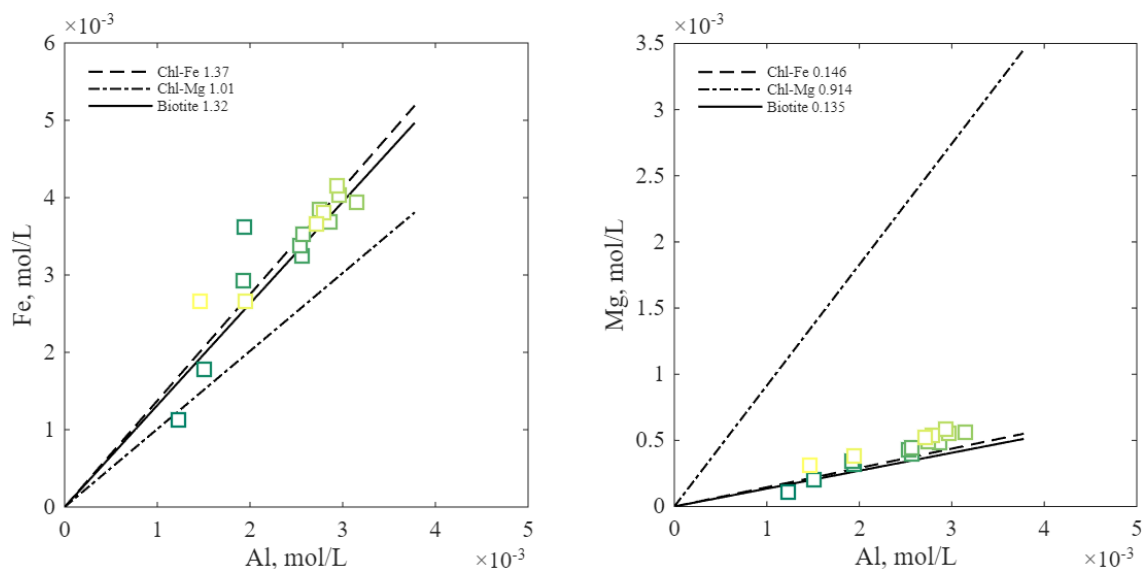


Figure 28 Stoichiometric relationships between experimentally measured and theoretical major-element concentrations for Experiment 2: Fe-Al and Mg-Al relationships for biotite and chlorite.

The stoichiometric results from Experiments 1 and 2 show broadly similar trends, but differences in the measured elemental concentrations indicate a change in the extent of mineral dissolution between the two experimental conditions. In both experiments, the measured La and Nd concentrations are generally higher than the theoretical contributions calculated for individual REE-bearing minerals, suggesting that the dissolved REEs likely originated from more than one mineral phase. The Fe concentrations show a closer agreement with the predicted dissolution of biotite and chlorite, supporting the contribution of these Fe-bearing silicates to the experimental solutions. The observed results in plots represent the stoichiometric dissolution.

A notable difference is observed for Nd, for which Experiment 2 shows a stronger deviation from the theoretical mineral dissolution trends. This indicates a relatively greater release of Nd under the conditions of Experiment 2. The Fe and Mg results, in contrast, remain relatively close to the biotite and chlorite predictions in both experiments, although the Mg concentrations are consistently much lower than the theoretical chlorite-Mg contribution.

3.4.2 Mineral dissolution rates calculations

The calculated mineral dissolution rates at 100 °C are presented in Figure 29. The literature-based dissolution-rate curves are compared with the experimental dissolution-rate values obtained in this study at the corresponding pH conditions. The comparison was performed for the biotite-chlorite system and for the REE-bearing bastnaesite-monazite system. These minerals were chosen because of the stoichiometric analysis.

For biotite and chlorite (Figure 29(a)), both literature-based dissolution rates show a similar decreasing trend with increasing pH. The calculated rates decrease from approximately $\log_{10}(r)=-12.7$ at pH 1 to approximately -15.1 at pH 6. The biotite and chlorite curves are very close to each other over the entire investigated pH range, indicating similar predicted pH dependence under the applied conditions. In contrast, the two experimental dissolution-rate values obtained in this study, at pH 2.16 and 3.49, are approximately $\log_{10}(r)=-10.7$. These values are therefore substantially higher than the literature-based rates, by approximately two to four orders of magnitude depending on pH.

For the REE-bearing mineral system (Figure 29(b)), the literature-based monazite dissolution rate also decreases systematically with increasing pH, from approximately -13.2 at pH 1 to approximately -16.7 at pH 6. The experimental bastnaesite dissolution rates obtained at pH 2.16 and 3.49 are approximately -10.1 and -10.2, respectively. These experimental values are considerably higher than the literature-based monazite dissolution rates over the investigated pH range.

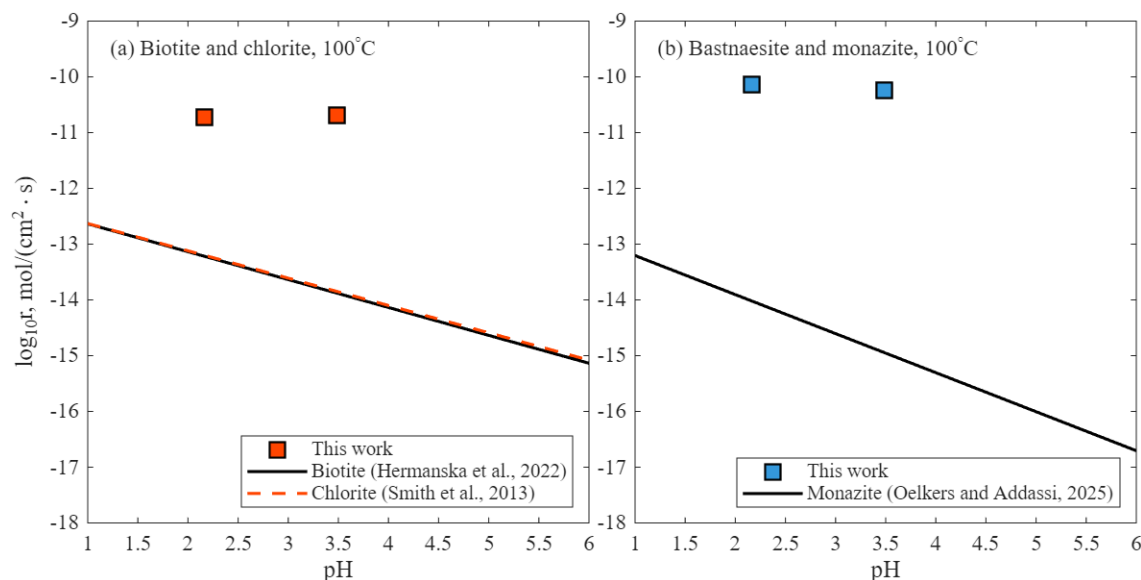


Figure 29 Comparison of experimental and literature-based mineral dissolution rates at 100 °C as a function of pH: (a) biotite and chlorite and (b) bastnaesite and monazite.

Overall, the experimental dissolution-rate values are consistently higher than the literature-based predictions for both mineral systems. The difference is particularly pronounced at the experimental pH values, where the experimental rates exceed the corresponding literature-based rates by several orders of magnitude. This discrepancy may be related to differences between the mineral surfaces investigated in this study and those used to derive the literature kinetic parameters, including differences in mineral composition, grain size, surface area, alteration state, and the presence of defects or highly reactive surface sites.

The comparison also demonstrates that literature-derived kinetic parameters provide a useful reference for the expected pH dependence of mineral dissolution but may not fully reproduce the dissolution behaviour of the investigated tailings material. In particular, the higher experimental rate obtained for bastnaesite relative to the literature-based monazite reference indicates that the REE-bearing mineral fraction may be more reactive under the experimental conditions than predicted from the monazite kinetic model. Therefore, the dissolution-rate comparison alone is not sufficient to evaluate the selectivity of the extraction process. The extent of elemental release is

further assessed using the experimental ICP-MS results and the PHREEQC modelling presented in the following sections.

3.4.3 Mineral saturation indexes

At 100 °C and pH 2 (Figure 30), several minerals showed positive SI values, indicating a potential for precipitation. The highest SI values were calculated for kaolinite (8.18), Ca-nonttronite (6.08) and Mg-nonttronite (5.83). Quartz also showed positive saturation with an SI of 1.20. Lower positive values were obtained for chalcedony (0.96), cristobalite (0.89), pyrophyllite (0.53), SiO₂(a) (0.48), K-nonttronite (0.38) and SiO₂(am) (0.25). Although some of these values are below 1, they are still positive and therefore indicate supersaturation and a thermodynamic possibility of precipitation.

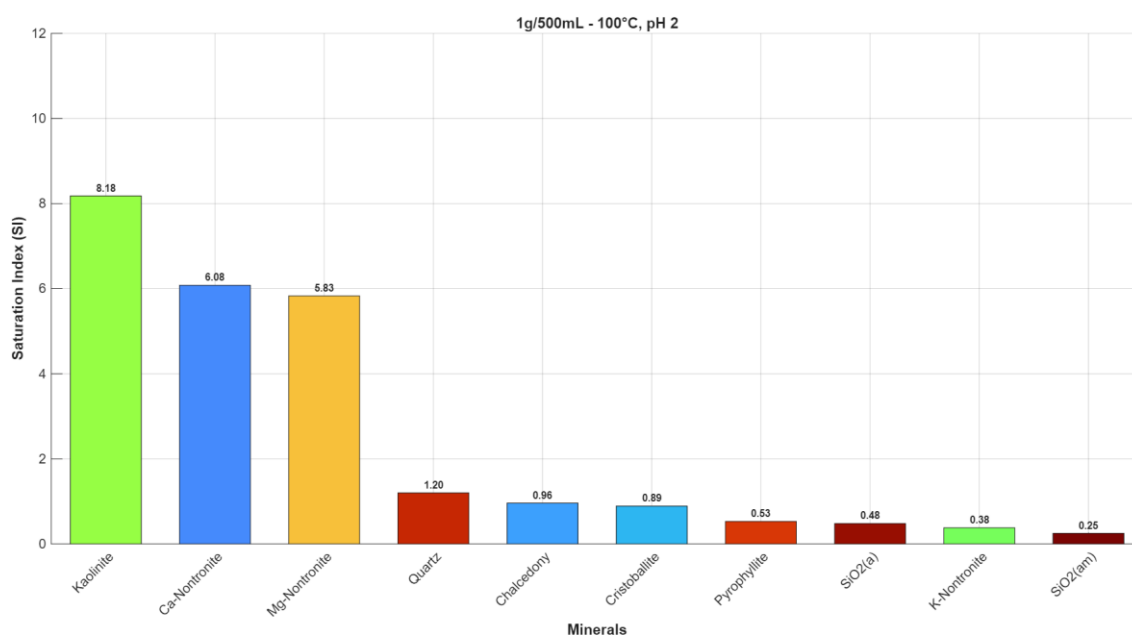


Figure 30 Calculated saturation indices (SI) of mineral phases at 100 °C and pH 2 (1 g/500 mL).

At 100 °C and pH 3 (Figure 31), a larger number of mineral phases showed positive SI values. The highest values were calculated for Ca-nonttronite (10.01), Mg-nonttronite (9.75), lepidolite (9.26), muscovite (7.89) and kaolinite (7.51). Other minerals, including pyrophyllite (5.88), halloysite (4.90), K-nonttronite (4.31), Na-nonttronite (3.79),

magadiite (2.79), diaspore (2.66) and hematite (2.24), also showed positive SI values. Several phases had values close to 1, such as quartz (1.21), chalcedony (0.96) and cristobalite (0.90), indicating relatively low supersaturation compared with the phases having higher SI values.

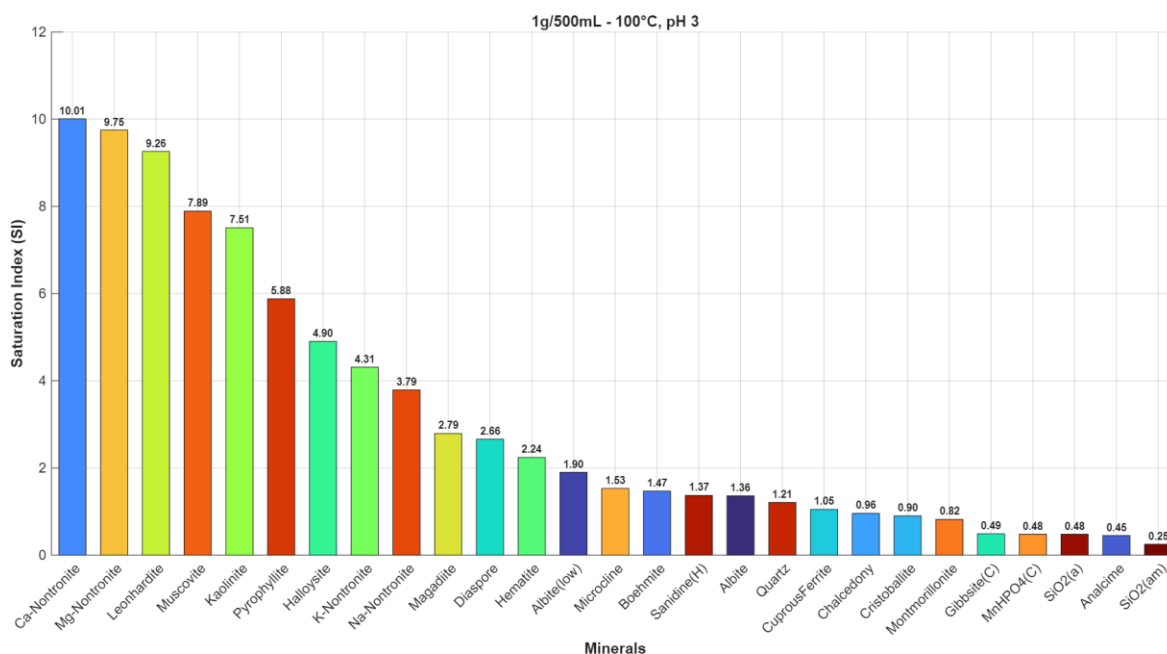


Figure 31 Calculated saturation indices (SI) of mineral phases at 100 °C and pH 3 (1 g/500 mL)

The PHREEQC results indicate that the simulated solutions were supersaturated with respect to several secondary mineral phases under both pH conditions. The higher number of minerals with positive SI values at pH 3 suggests that the aqueous composition at this condition favors the formation of a wider range of secondary phases.

However, positive SI values represent thermodynamic predictions and do not necessarily mean that precipitation actually occurred during the experiments. A positive SI indicates that precipitation is thermodynamically favorable, but the actual formation of a mineral also depends on reaction kinetics and the duration of the experiment. Therefore, the PHREEQC results were used to identify possible secondary mineral phases and to evaluate the expected geochemical behavior of the solutions during the dissolution experiments (Parkhurst and Appelo, 2013).

4 Summary, conclusions and outlook

4.1 Summary and conclusions

The results of this study show that the investigated mine-tailings material is highly reactive under the tested conditions. Both experiments resulted in substantial dissolution of several major and trace elements, while the extraction of most REEs remained moderate to low. The comparison between pH 2 and pH 3 also showed that pH affects the mobilization of individual elements differently, indicating that it can be used to influence the selectivity of the process.

A key outcome of the study is that the experimental dissolution rates were considerably higher than those predicted from literature-based kinetic parameters. This indicates that the studied material is more reactive than expected and that the conditions applied were too aggressive for the objective of controlled dissolution.

Therefore, although the experiments successfully demonstrated effective dissolution, they also showed that maximizing element release is not the main objective. Based on these results, the experimental strategy should be adjusted towards lower temperatures and higher pH values. These conditions are expected to slow the dissolution process and provide a better basis for identifying a suitable range for selective extraction.

4.2 Future work

Future experiments should focus on reducing the aggressiveness of the dissolution conditions and improving the selectivity of the process. Based on the high reactivity observed in the present experiments, the experimental strategy should be modified by using lower temperatures and higher pH values. Lowering the temperature should reduce the overall dissolution rate, while increasing the pH should further decrease acid-promoted dissolution. A gradual increase in pH, starting from the conditions tested in

this study, would allow the response of the material to be evaluated over a wider range of less acidic conditions.

The experimental results should also continue to be combined with geochemical modelling to evaluate mineral stability and possible secondary mineral formation under the new conditions. Additional experiments with different reaction times could help identify the stage at which sufficient target-mineral dissolution is achieved without excessive dissolution of associated phases.

Ultimately, the aim of the next stage of the project should be to identify an operating window that provides controlled and selective dissolution rather than maximum dissolution. The results observed in this study provide a useful starting point for defining further experimental strategy and demonstrate the importance of adapting the experimental conditions to the specific behavior of the investigated mine-tailings material.

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