

## Article

# Effects of Ammonium Salts on Rare Earth Leaching Process of Weathered Crust Elution-Deposited Rare Earth Ores

Zhenyue Zhang <sup>1,2</sup>, Changyu Zhou <sup>1</sup>, Wendou Chen <sup>1,2,\*</sup>, Fei Long <sup>1,2</sup>, Zhuo Chen <sup>1,2</sup> and Ru'an Chi <sup>1,2</sup><sup>1</sup> School of Resources & Safety Engineering, Wuhan Institute of Technology, Wuhan 430073, China<sup>2</sup> Key Laboratory for Green Chemical Process of Ministry of Education, Wuhan Institute of Technology, Wuhan 430073, China

\* Correspondence: 12117010002@stu.wit.edu.cn; Tel.: +86-135-4039-6660

**Abstract:** In order to reveal the influence of ammonium salts on the rare earth leaching process of weathered crust elution-deposited rare earth ores, ammonium acetate, ammonium chloride, and ammonium sulfate were used as leaching agents. The effects of the leaching agent on the rare earth leaching efficiency and the expansion, dissolution, and transformation behavior of clay minerals in the rare earth leaching process were studied. The results showed that rare earth leaching efficiency followed the order ammonium acetate > ammonium chloride > ammonium sulfate, with values of 90.60%, 85.96%, and 84.12%, respectively. The swelling ratio of clay mineral followed the order ammonium acetate < ammonium chloride < ammonium sulfate; the clay mineral swelling ratio was 2.09% when ammonium acetate was the leaching agent. Thermogravimetric analysis showed that the interlayer water content was the lowest when ammonium acetate was used as the leaching agent. Under the conditions of different leaching agents, the clay mineral contents changed from illite and halloysite to smectite and kaolinite. When ammonium acetate was used as the leaching agent, the relative conversion of illite was 1.49%, and that of smectite was only 0.17%. SEM analysis showed that the clay minerals expanded and dissolved obviously when ammonium chloride and ammonium sulfate were used as the leaching agents. Meanwhile, the clay mineral layered structure was relatively complete when ammonium acetate was used as the leaching agent. Therefore, when ammonium acetate was used as the leaching agent, it had the least effect on the swelling, dissolution, and transformation of clay minerals. This can provide a theoretical basis for the safe production of weathered crust elution-deposited rare earth ore, and for the screening of green and efficient leaching agents.

**Keywords:** weathered crust elution-deposited rare earth ores; ammonium salts; leaching efficiency; swelling ratio; clay minerals



**Citation:** Zhang, Z.; Zhou, C.; Chen, W.; Long, F.; Chen, Z.; Chi, R. Effects of Ammonium Salts on Rare Earth Leaching Process of Weathered Crust Elution-Deposited Rare Earth Ores. *Metals* **2023**, *13*, 1112. <https://doi.org/10.3390/met13061112>

Academic Editor: Corby G. Anderson

Received: 22 May 2023

Revised: 10 June 2023

Accepted: 12 June 2023

Published: 13 June 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

As an extremely important non-renewable mineral resource, rare earth plays a vital role in global economic development [1–3]. In particular, the medium and heavy rare earth elements, represented by terbium and lutetium, show high economic value and are extremely scarce. At present, the world's medium and heavy rare earth ores mainly come from the mining of weathered crust elution-deposited rare earth ore. The weathered crust elution-deposited rare earth ores are formed by the chemical weathering of various bedrocks [4,5] and are widely distributed in warm and moist regions, predominantly in southern China [6–8]. Rare earth elements mainly exist in the ionic or hydration ionic state on the surface of the clay minerals [9–11]. It is difficult to recover this type of rare earth ore using conventional beneficiation methods, and rare earth is normally recovered using an ion exchange method, and by adding electrolyte solution [12,13]. The leaching process of weathered crust elution-deposited rare earth ore has successively developed the process of sodium chloride barrel leaching, ammonium sulfate bath leaching/heap leaching, and

ammonium sulfate in situ leaching to recover rare earth [14–16]; the problems of rare earth recovery from weathered crust elution-deposited rare earth ore have thus been solved effectively. However, the mining of weathered crust elution-deposited rare earth ore is accompanied by a series of problems, such as hydration expansion, dissolution, and the transformation of clay minerals [17,18]. This mining can easily cause geological disasters such as landslides, which brings serious safety risks to mine production [19,20].

Many researchers have been engaged in long-term research on the reason for landslides in ore areas. Liu et al. [21] studied the constraints of mineral evolution on REE enrichment and differentiation during weathering and eluviation. It was found that the ion-exchanged REE contents increased from bedrock to the REE-enriched layer, and hornblende and biotite were gradually transformed into illite, montmorillonite, kaolinite, and halloysite with the enhancement of weathering. Jin [22] found the migration and transformation rule of clay minerals in the leaching process. The ammonium sulfate solution was continuously injected into the profile, as acidic ammonium sulfate solution can promote the transformation of feldspar and clay minerals. Hydrogen ions in the solution will react with potassium feldspar in rare earth ores. Under the action of hydrogen ions and water, the potassium feldspar will lose potassium ions and form kaolinite or illite. Wang et al. [23] used organic acid containing a carboxyl group and ammonium chloride as leaching agents to study the interaction mechanism between the carboxyl group and rare earth ions in the rare earth leaching process. The results showed that the complexation between  $RE^{3+}$  and  $-COO^-$  was dominant in the solution of  $C-COOH > 2.0$  m mol/L, which is beneficial for the leaching of rare earths, while  $-COO^-$  mainly changes the surface electrical properties of clay minerals in the solution of  $C-COOH < 2.0$  m mol/L. However, the weathered crust elution-deposited rare earth ore is a typical clay mineral, and there are few reports on the evolution of clay minerals in the leaching process. The action of the leaching agent makes clay minerals expand, dissolve, and transform, which weakens the local stability of rare earth ore bodies. The hydration expansion effect can affect the ion exchange reaction between REE ions and leaching agent cations on the clay mineral surface, which is not conducive to the efficient recovery of the rare earth in situ leaching process. Therefore, it is of great significance to study the swelling, dissolution, and transformation of clay minerals during the rare earth leaching process.

In this paper, the influence of ammonium salts on the swelling, dissolution, and transformation of clay minerals during the rare earth leaching process was studied. It has a certain guiding significance for the safety production of weathered crust elution-deposited rare earth ore, and provides a theoretical basis for screening green and efficient leaching agents.

## 2. Materials and Methods

### 2.1. Chemical Composition of the Rare Earth Ores

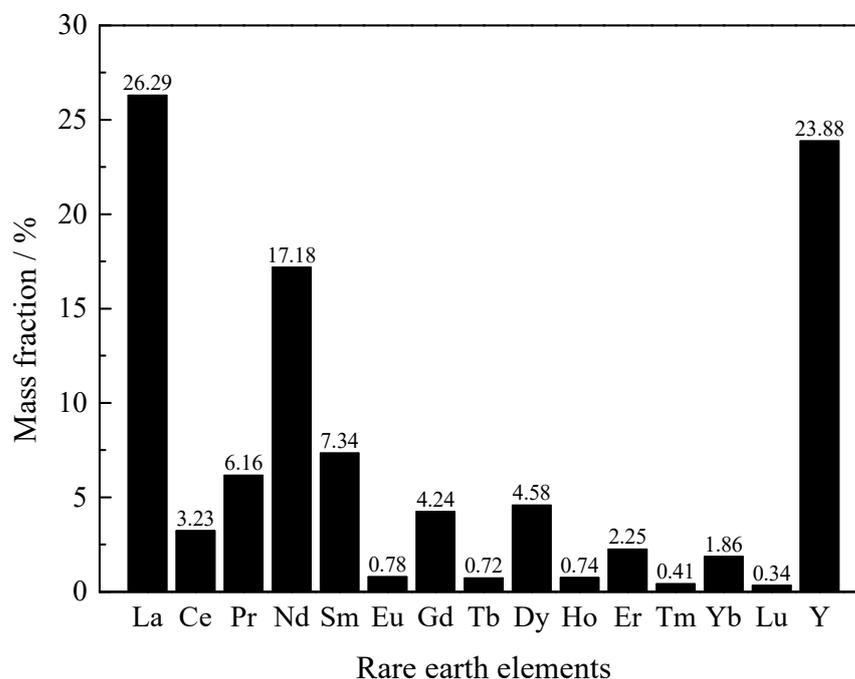
The ore samples were collected from Fujian Province, China. The chemical composition of the rare earth ore was analyzed via an X-ray fluorescence spectrometer, and the results are shown in Table 1.

**Table 1.** Chemical composition of ore samples/%.

Components	REO	Al <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	MnO <sub>2</sub>	ZnO	MgO
Content	0.112	31.808	0.106	60.796	0.386	0.018	0.541
Components	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	SO <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Rb <sub>2</sub> O	LOSS
Content	0.109	1.569	0.188	0.098	1.058	0.038	3.173

It can be seen from Table 1 that SiO<sub>2</sub> was the leading compound within the ore sample, occupying 60.796%. The amounts of Al<sub>2</sub>O<sub>3</sub> and REO were 31.808% and 0.112%, respectively. Rare earth partitioning is an important index to evaluate the industrial value of the rare

earth ore. The rare earth partitioning of the ore sample was analyzed via ICP-MS, as shown in Figure 1.



**Figure 1.** The rare earth elements partitioning of the rare earth ores.

As can be seen from Figure 1, the content of light rare earths was 52.89% of the total rare earth content. The remaining medium and heavy rare earths accounted for 47.11%. The contents of terbium, dysprosium, and lutetium were 0.72%, 4.58%, and 0.34%, respectively, which were higher than the standard ore value, indicating the high utilization value of rare earth.

## 2.2. Experimental Methods

### 2.2.1. Experimental Equipment and Methods

All the chemicals in this study were of analytical grade. In total, 100.00 g of dried ore sample was put into a beaker using a quartering method. Ammonium salt leaching agents with a concentration of 0.20 mol/L were added at a liquid–solid ratio of 2:1, and the leaching agents were stirred at a rotational speed of 240 r/min, as shown in Figure 2. The rare earth concentrations were determined using ICP-MS. Ore samples' zeta potentials were detected by the Zetasizer Nano. The thermal gravimetric analyzer was used to analyze the ore sample water contents. The temperature growth rate was 10 °C/min, the protective gas was nitrogen, and the test temperature range was 30~1000 °C. The PCY-type intelligent clay dilatometer (as shown in Figure 3) was used to detect the swelling ratio of clay minerals, which was represented by  $\delta$ . The swelling ratio of the ore sample was measured using the following formula [24]:

$$\delta = \Delta H / H_0 \times 100\% \quad (1)$$

where  $\Delta H$  is the change in height, and  $H_0$  is the original height of the sample.

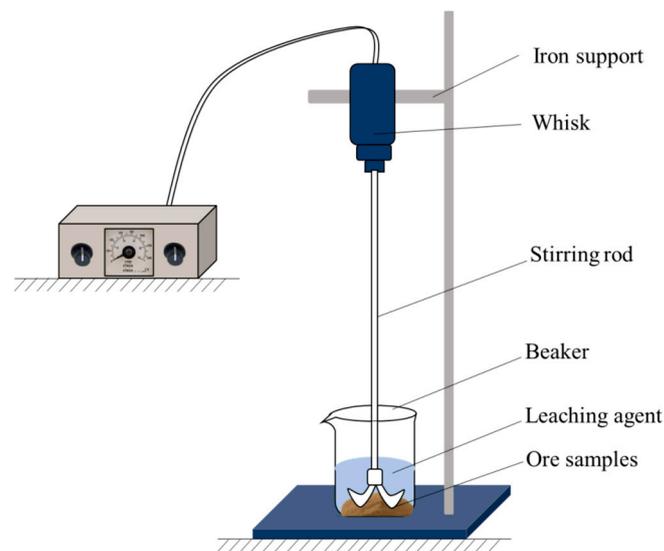


Figure 2. The self-made agitation leaching device.

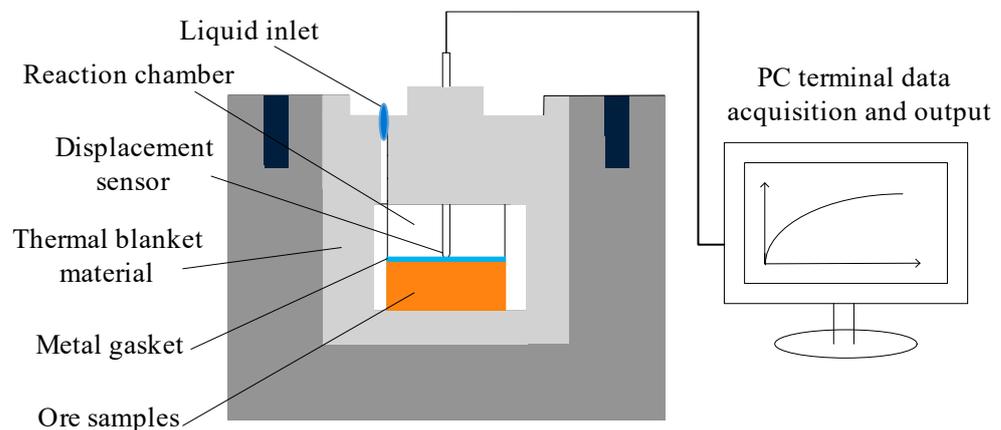


Figure 3. The PCY intelligent clay dilatometer.

### 2.2.2. Extraction and Calculation of Clay Minerals

Clay minerals were extracted according to the Stokes sedimentation principle. Directional slices were prepared via the scraping method. X-ray diffraction (XRD) tests were conducted on the oriented thin sheets under a natural environment (N), ethylene glycol environment (EG), heating environment (T), and dimethyl sulfoxide environment (DMSO). The test conditions were copper target (Cu-K $\alpha$  radiation), scanning Angle of 5°–60°, and scanning speed of 2.4°/min [25]. The quantification method of clay minerals was performed according to the analysis method for clay minerals and ordinary non-clay minerals in sedimentary rocks by the X-ray diffraction (SY/T 5163-2018). The contents were calculated using the following equations:

$$Kao - group = \frac{I_{0.7nm}(N)/1.5}{I_{0.7nm}(N)/1.5 + I_{0.7nm}(T)} \times 100 \quad (2)$$

$$It = \frac{I_{1.0nm}(EG) \times [h_{0.7nm}(N)/h_{0.7nm}(EG)]}{I_{1.0nm}(T)} \times (100 - Kao) \quad (3)$$

$$S = 100 - Kao - It \quad (4)$$

The clay minerals of the kaolinite group, and kaolinite, halloysite, illite and smectite were expressed by *Kao-group*, *Kao*, *Hal*, *It*, and *S*, respectively.

The relative content of kaolinite and halloysite in the kaolinite group can be calculated as [26]

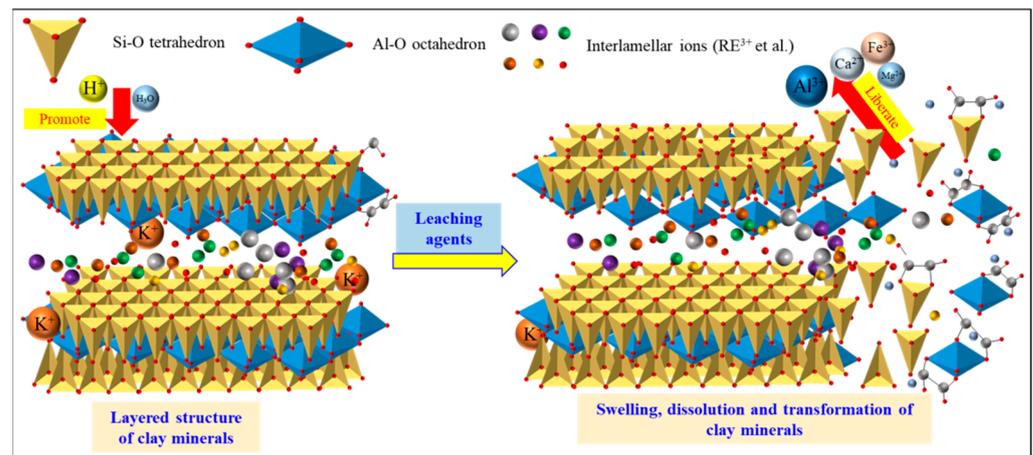
$$\frac{Hal}{Kao} = K \frac{I_{1.09nm}(DMSO)}{I_{0.715nm}(DMSO)} \quad (5)$$

where  $h$  is the change in height of the diffraction peak in the XRD pattern, and  $I$  is the intensity of the diffraction peaks in an XRD pattern, and the subscript represents the position of the diffraction peak in the spectrum.  $N$ ,  $EG$ , and  $T$  represent the diffraction peaks of different directional plates. Take the same amount of halloysite and kaolinite standard samples mixed with dimethyl sulfoxide for 5 h, measure the  $d_{001}$  diffraction peak intensity, respectively, and the ratio is  $K$ .

### 3. Results and Discussions

#### 3.1. Model of Clay Mineral Transformation during Rare Earth Leaching Process

The leaching process of the weathered crust elution-deposited rare earth ore includes the ion exchange process, and the swelling and dissolution of clay minerals. Compared with the weathering process in natural mineralization, the leaching process of the weathered crust elution-deposited rare earth ore can be regarded as a kind of artificial weathering process. Adding different leaching agents in the rare earth leaching process leads to a series of effects on the swelling and dissolution of clay minerals. The process is illustrated in Figure 4.



**Figure 4.** Model of clay mineral transformation during rare earth leaching process.

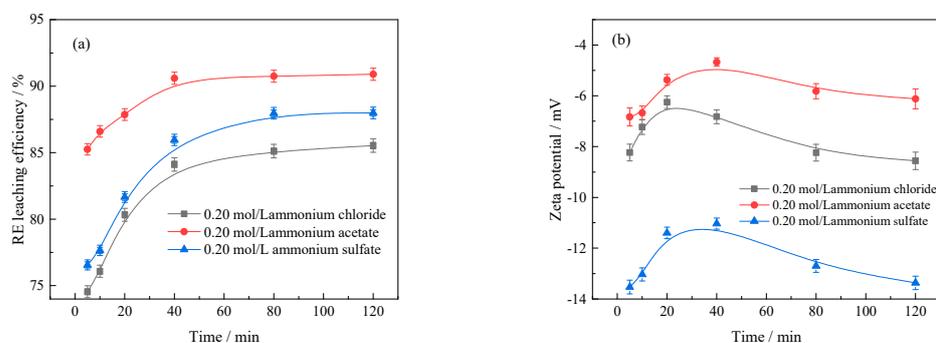
The clay minerals in weathered crust elution-deposited rare earth ore mainly include halloysite, kaolinite, illite, and montmorillonite. The rare earth elements mainly exist in the ionic or hydration ionic state on the surface of the clay minerals [27]. When clay minerals were placed in a solution environment, rare earth ions and parts of impurity ions were replaced into the solution under the action of the leaching agent. With the extension of the leaching time, the clay minerals will further expand, dissolve, and transform [28], resulting in the release of  $Al^{3+}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Fe^{3+}$ , and  $K^{+}$  into the solution. Therefore, the structure of clay minerals is transformed to some extent. In this paper, the effects of ammonium salt leaching agents on rare earth leaching, and clay mineral swelling, dissolution, and transformation were studied.

#### 3.2. Effects of Ammonium Salts on Rare Earth Leaching Process

##### 3.2.1. Effects of Ammonium Salts on Rare Earth Leaching Efficiency

In order to explore the effects of ammonium salt leaching agents on the rare earth leaching efficiency, 0.20 mol/L ammonium acetate, ammonium sulfate, and ammonium chloride were used as leaching agents. The rare earth leaching solution at different time periods was collected, the rare earth leaching efficiency was calculated, and the zeta

potential of the mineral surface was detected. The rare earth leaching process is the process of the ion exchange reaction between rare earth ions and leaching agent cations, and the occurrence of this process was accompanied by a change in zeta potential on the surface of the clay minerals. Therefore, it was necessary to discuss the change in zeta potential on the surface of the clay minerals while exploring the rare earth leaching efficiency. The results are shown in Figure 5.



**Figure 5.** Effect of leaching agents on leaching efficiency and zeta potential of rare earth ores. (a) Rare earth leaching efficiency; (b) zeta potential.

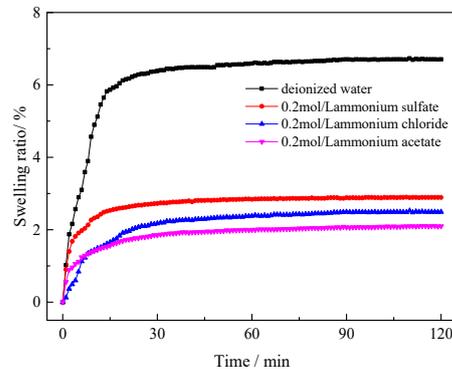
It can be seen from Figure 5a that the rare earth leaching efficiency gradually increased in the first 40 min and tended to be stable after 40 min. The order of rare earth leaching efficiency was ammonium acetate > ammonium sulfate > ammonium chloride, with values of 90.60%, 85.96%, and 84.12%, respectively. It can be seen from Figure 5b that the absolute value of the zeta potential of the mineral surface gradually decreased in the first 40 min of rare earth leaching because the rare earth ions and electrolyte cations occurred obviously in the ion exchange reaction at this stage. The electric double layer was compressed and the thickness of the electric double layer was reduced, resulting in a decreased zeta potential [29]. When ammonium sulfate was used as the leaching agent, the absolute value of zeta potential was the largest, which means that the ammonium sulfate had more negative charges than the other leaching agents. When the leaching process was carried out for 40 min, the rare earth leaching reaction tended to be balanced, the ion exchange reaction intensity was weakened, and, under the action of the leaching agent, the clay mineral water molecules entered the interlayer space of the clay minerals, leading to an increase in the interlayer spacing and number of layers of clay minerals. This results in the dissolution of mineral cations and an increase in the negative zeta potential of the mineral surface. The zeta potential, with a relatively small absolute value, generates less charge on the surface of clay minerals, which was directly related to the expansion of clay minerals. The results showed that the absolute value of the zeta potential was the smallest when ammonium acetate was used as the leaching agent, indicating that ammonium acetate had the least effect on clay minerals.

### 3.2.2. Effects of Ammonium Salts on Swelling Ratio of Clay Minerals

In order to explore the effects of leaching agents on the swelling ratio of clay minerals in the rare earth leaching process, the clay mineral swelling ratios in deionized water, ammonium chloride, ammonium sulfate, and ammonium acetate solutions were calculated. The results are shown in Figure 6.

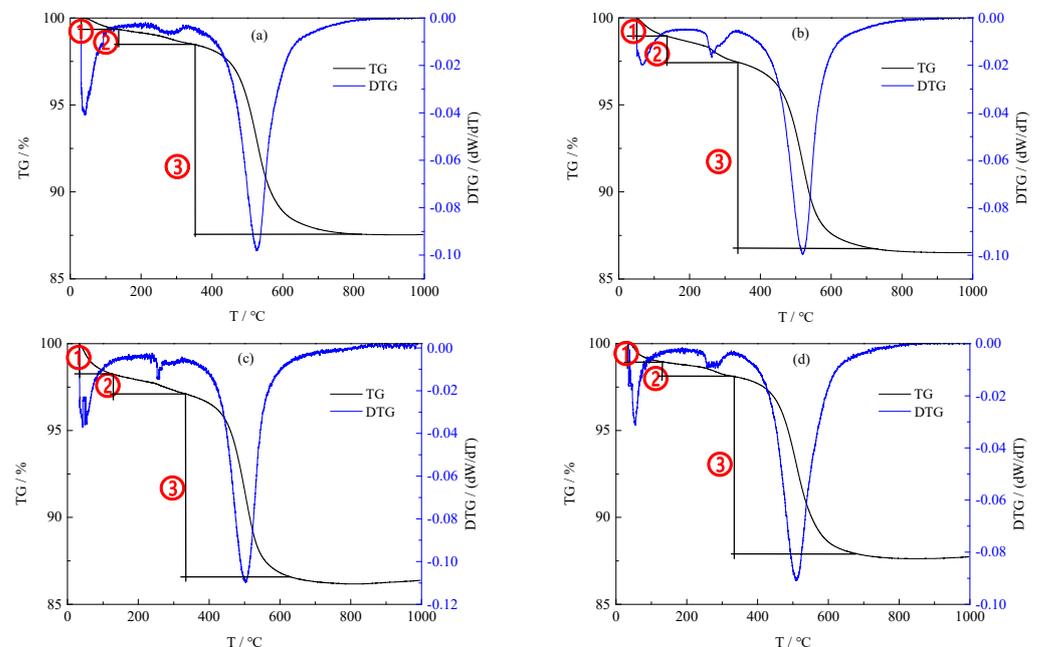
It can be seen from Figure 6, during the rare earth leaching process, that the swelling ratio of clay minerals gradually increased, and the swelling process balanced after 30 min. The swelling ratios of clay minerals under different leaching agents followed the order  $\delta_{\text{deionized water}} > \delta_{\text{ammonium sulfate}} > \delta_{\text{ammonium chloride}} > \delta_{\text{ammonium acetate}}$ , with values of 6.71%, 2.89%, 2.50%, and 2.09%, respectively. It can be seen that in the rare earth leaching process, three kinds of leaching agents can inhibit the swelling of clay minerals to a certain extent, and the swelling inhibition effect is most obvious when ammonium acetate

is used as the leaching agent. The hydration and swelling of clay minerals are mainly caused by water molecules entering the interlayer structure of clay minerals. After adding ammonium acetate solution, acetate ions can be adsorbed at the edge of clay mineral particles. Therefore, the originally hydrophilic clay mineral surface was changed into a relatively hydrophobic one, which can effectively prevent water molecules from entering the interlayer structure of clay minerals, reducing the swelling ratio of clay minerals [30].



**Figure 6.** Effect of leaching agents on swelling ratio of clay minerals.

The evolution of clay minerals always occurred in contact with pore water, and the formation transformation of clay minerals was controlled by the leaching of aqueous medium [31–33]. In order to verify the transformation of clay minerals in the rare earth leaching process, the water retention properties of ore samples after the action of different leaching agents were analyzed using a thermogravimetric analyzer. The differences in the adsorption water relative contents, interlayer water, and constitution water of clay minerals were discussed, and the results are shown in Figure 7 and Table 2.



**Figure 7.** Thermogravimetric curves of ore samples under different leaching agents. (a) Raw ore; (b) ore sample with the ammonium chloride as leaching agent; (c) ore sample with the ammonium sulfate as leaching agent; (d) ore sample with the ammonium acetate as leaching agent; ① ② ③ represents the three weightless regions of the ore sample.

**Table 2.** Ore sample weight loss ratio/%.

Ore Sample	Weight Loss Ratio		
	Region 1	Region 2	Region 3
Raw ore	0.65	0.88	10.71
Ammonium chloride	1.16	1.29	10.33
Ammonium sulfate	1.70	1.41	10.51
Ammonium acetate	1.05	0.85	10.59

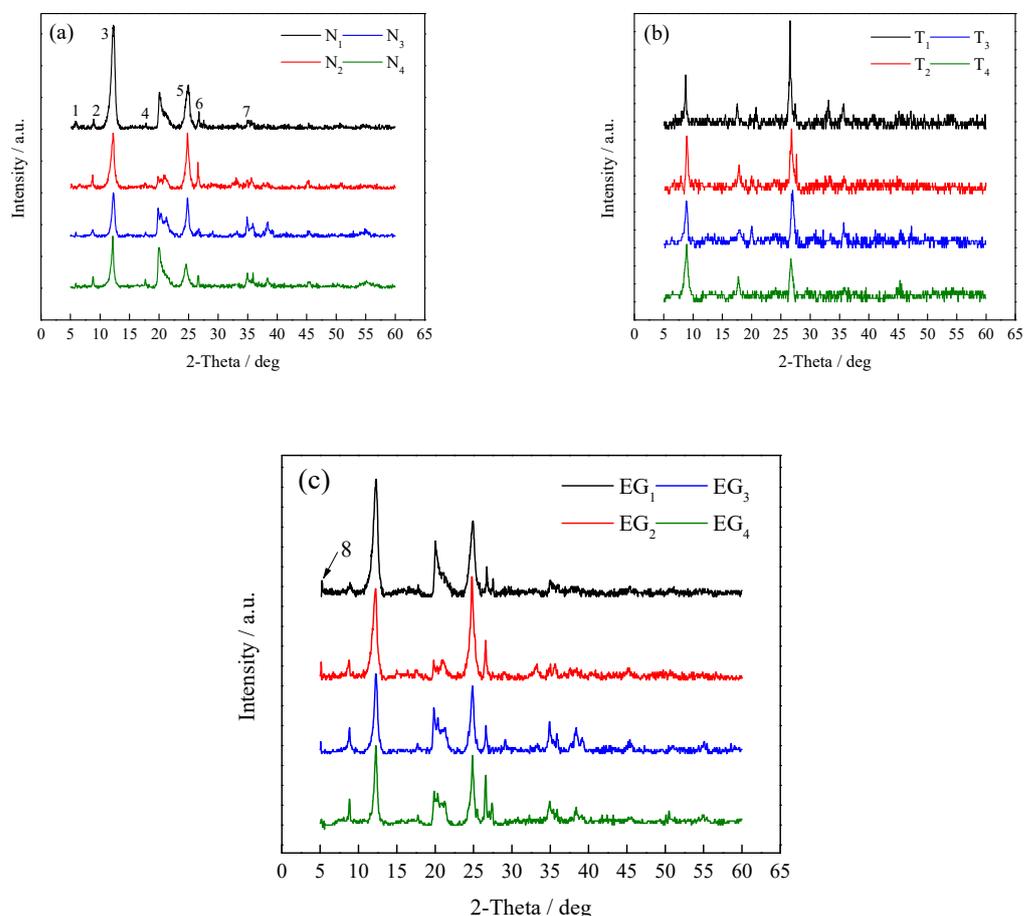
The experimental data were from the same batch of ore samples, using the same experimental method. After three tests at different times, the experimental error was less than 0.15%, and the average value was taken to represent the experimental results. It showed that the reproducibility of data was good. It can be seen from Figure 7 that all ore samples had three obvious weight loss peaks, which represented the adsorption water, interlayer water, and constitution water lost from clay minerals. The first range was 30~120 °C, in which the adsorption water on the surface of clay minerals and the weakly bound interlayer water were removed. The second range was 120~330 °C, and the interlayer water that was strongly combined was removed. The third weight loss interval was 330~600 °C, where the constitution of the water between crystal lattices with the strongest binding force was lost. This part of the water was mainly involved in forming mineral lattices in the form of OH<sup>-</sup> or H<sub>3</sub>O<sup>+</sup> [32]. It can be seen from Table 2 that after adding different leaching agents, the weight loss rate of water in region 1 and region 2 of clay minerals changed obviously, while that in region 3 had little change. When ammonium chloride was used as the leaching agent, the surface bound water (region 1) content was 1.16%, and the interlayer bound water (region 2) content was 1.29%. When ammonium sulfate was used as the leaching agent, the content of surface bound water (region 1) was 1.70%, and the interlayer bound water (region 2) was 1.41. When ammonium acetate was used as the leaching agent, the surface bound water (region 1) content was 1.05%, and the interlayer bound water (region 2) was 0.82%, which is close to the raw ore. In conclusion, when ammonium chloride and ammonium sulfate were used as leaching agents, the content of clay-mineral-bound water was far greater than that in raw ore, while when ammonium acetate was used as the leaching agent, the content of bound water was closest to raw ore. Therefore, the expansion, dissolution, and transformation of clay minerals were minimal when ammonium acetate was used as the leaching agent.

### 3.3. Effects of Ammonium Salts on Clay Minerals in Rare Earth Leaching Process

To study the evolution of clay minerals during the rare earth leaching process, rare earth tailings treated with different leaching agents were collected, and the relative contents of clay minerals in the tailings were analyzed using X-ray diffraction and the K value method. The results are shown in Figure 8.

It can be seen from Figure 8a that the characteristic peaks of kaolinite-group clay minerals in the natural sheet were  $d_{001} = 7.15 \text{ \AA}$ ,  $d_{002} = 3.57 \text{ \AA}$ , and  $d_{003} = 2.34 \text{ \AA}$ , respectively, corresponding to peaks 3, 5, and 7 in Figure 8a. However, their characteristic peaks will disappear due to lattice damage under a high temperature. As can be seen from the high-temperature heating slice in Figure 8b, the characteristic peak of the kaolinite-group clay disappears. The characteristic peaks of illite in the natural slice were  $d_{001} = 10 \text{ \AA}$ ,  $d_{002} = 5 \text{ \AA}$ , and  $d_{003} = 3.33 \text{ \AA}$ , where the intensity of  $d_{002}$  was about 1/3 of that of  $d_{001}$ , corresponding to peaks 2, 4, and 6 in Figure 8a, respectively. The smectite interlamellar domains can accommodate varying amounts of water molecules and cations, and the characteristic peak  $d_{001}$  was not fixed, usually around 15 Å. It can be seen from the ethylene-glycol-saturated slice in Figure 8b that the ethylene glycol molecules entered the smectite interlayer domain, resulting in an increase in interlayer spacing, and the characteristic peak moved to the left. Therefore, it can be seen that the weak peak No.1 in the natural slice was the characteristic peak of smectite, while the corresponding peak in the ethylene-glycol-saturated sheet was

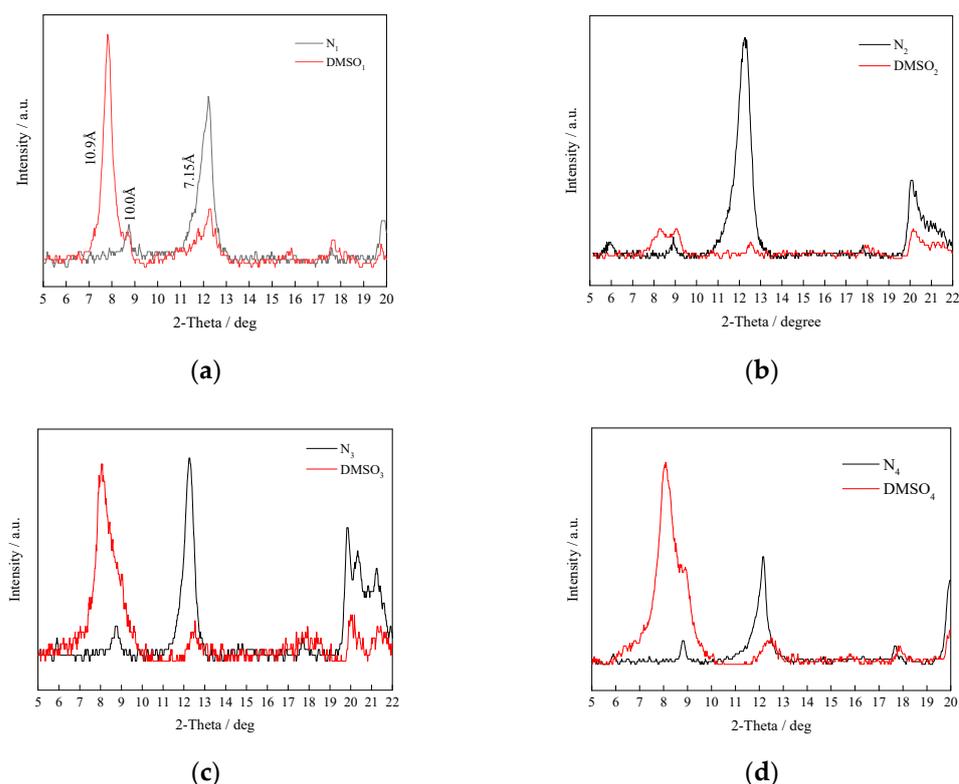
peak No.8. To sum up, the clay minerals in the samples included kaolinite-group clay minerals, illite and smectite [26].



**Figure 8.** The XRD patterns of clay mineral. (a) Natural sheets; (b) heated sheets; (c) ethylene-glycol-saturated sheets. N<sub>1</sub>–N<sub>4</sub> (T<sub>1</sub>–T<sub>4</sub>, EG<sub>1</sub>–EG<sub>4</sub>) represent the spectrum of raw ore, and tailings after the actions of ammonium chloride, ammonium sulfate and ammonium acetate.

The kaolinite group includes kaolinite and halloysite, with halloysite being subdivided into 7 Å halloysite and 10 Å halloysite. At room temperature, 10 Å halloysite easily loses part of the interlayer, and hydrates and transforms into 7 Å halloysite. To accurately calculate the relative content of kaolinite and halloysite, the natural slice can be saturated with dimethyl sulfoxide (DMSO). DMSO can enter the 7 Å halloysite layer structure and form an intercalation complex, so that the (001) layer spacing swelling occurs while the kaolinite layer structure is kept intact [17,26]. The XRD patterns of the DMSO slice are shown in Figure 9.

It can be seen from Figure 9 that after the sample was saturated with dimethyl sulfoxide, the intensity of  $d_{001} = 7.15 \text{ \AA}$  was weakened, and a new peak appeared at  $d = 10.9 \text{ \AA}$ . Thus, the clay minerals of the kaolinite group contain both halloysite and kaolinite [17,26]. The relative contents of clay minerals in different ore samples were analyzed and calculated, and the results are shown in Table 3.

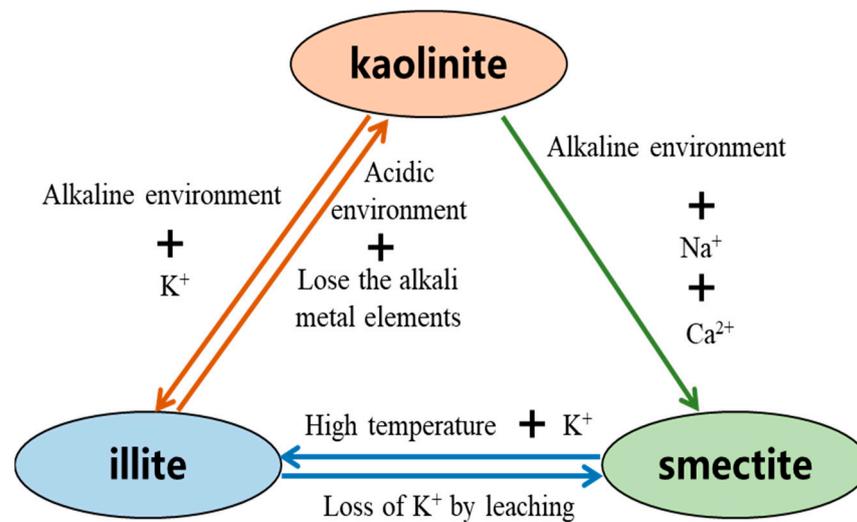


**Figure 9.** The XRD pattern of clay mineral natural slice and dimethyl sulfoxide slice.  $N_1$ – $N_4$  ( $DMSO_1$ – $DMSO_4$ ) (a–d) represent the spectrum of raw ore, and tailings after the action of ammonium chloride, ammonium sulfate, and ammonium acetate.

**Table 3.** The relative content of clay mineral in ore samples/%.

	Hal	Kao	It	S	$\Delta It$	$\Delta S$
Raw ore	67.39	20.05	10.64	1.92	0.00	0.00
Ammonium chloride	66.78	22.60	8.19	2.43	−2.45	0.51
Ammonium sulfate	66.01	22.85	7.40	3.74	−3.24	1.82
Ammonium acetate	66.39	22.37	9.15	2.09	−1.09	0.17

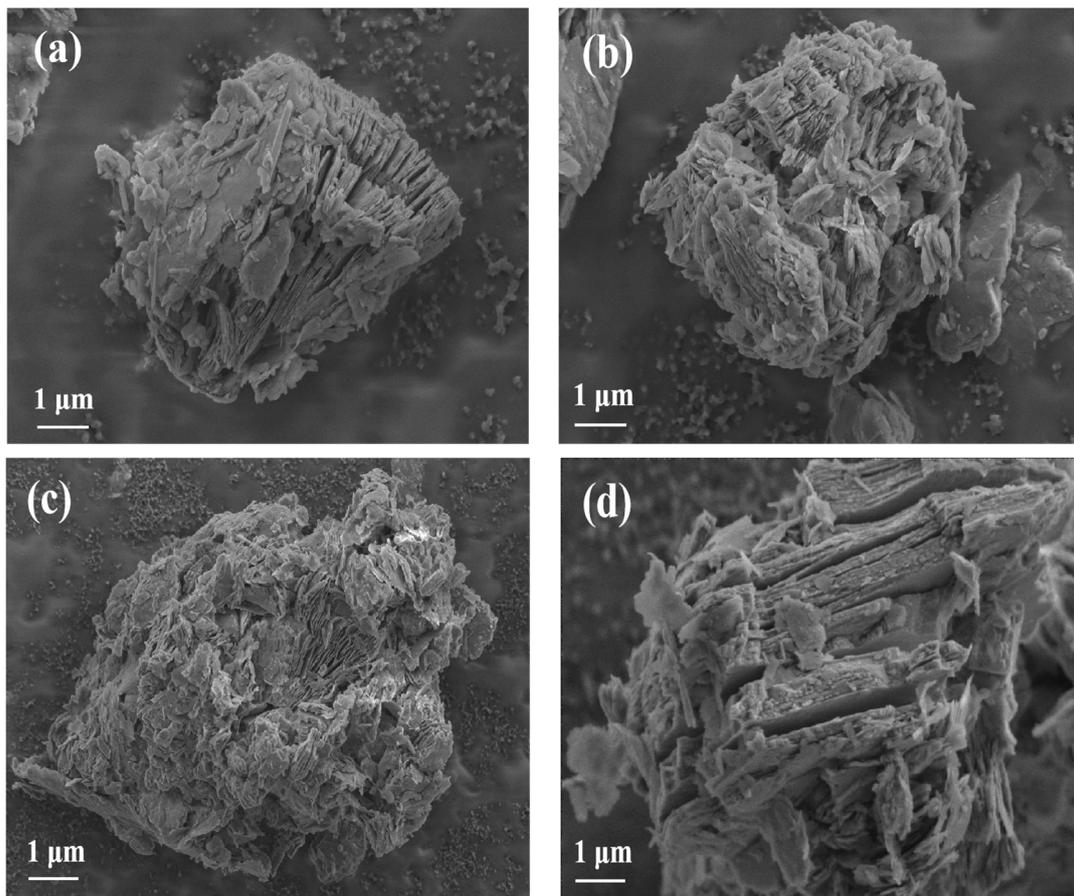
It can be seen from Table 3 that the main clay minerals in the ore sample were halloysite and kaolinite, followed by illite and smectite, accounting for 67.39%, 20.05%, 10.64%, and 1.92%, respectively. Under the action of different leaching agents, the relative content of clay minerals changed to some extent, especially illite. Under the action of leaching, the transformation of the 2:1 type illite was the easiest. The continuous loss of  $K^+$  in the illite crystal layer leads to illite evolving to montmorillonite. Meanwhile, when the alkali metal was removed in large quantities, the illite evolved further to form kaolinite [34]. This process is illustrated in Figure 10 [35]. It can be seen from Table 3 that the relative contents of kaolinite and smectite increased after the leaching process of the three ammonium salts, while the relative contents of illite decreased. When ammonium acetate was used as the leaching agent, the relative conversion rate of illite was 1.49% and that of smectite was only 0.17%. This also verified that the swelling ratio of clay minerals under the action of ammonium acetate was minimal.



**Figure 10.** Diagram of clay minerals mutual transformation.

#### 3.4. Scanning Electron Microscopy Analysis of Ore Sample

In order to explore the influence of the leaching agent on clay minerals, the raw ore and the tailings after leaching of three kinds of ammonium salts were detected and analyzed via a scanning electron microscope. The results are shown in Figure 11.



**Figure 11.** The SEM analysis of ore samples. (a) Raw ore; (b) ore sample with the ammonium chloride as leaching agent; (c) ore sample with the ammonium sulfate as leaching agent; (d) ore sample with the ammonium acetate as leaching agent.

It can be seen from Figure 11 that the surface morphology of clay minerals changed to a certain extent under the influence of the three leaching agents. As can be seen from Figure 11b, a certain degree of dissolution and transformation occurred in the clay minerals after the action of ammonium chloride. The surface morphology of clay minerals was eroded seriously, the layered structure of clay minerals was partially destroyed, and the clay mineral particles fell off along the layered structure. Therefore, there was a large number of interlayer ions released into the solution during the rare earth leaching process. As can be seen from Figure 11c, the clay minerals after ammonium sulfate leaching also showed a serious erosion phenomenon. However, the layered structure of the clay minerals only showed an obvious swelling phenomenon; the dissolution and detachment of the clay minerals were not obvious. It can be seen from Figure 11d that the clay minerals after ammonium acetate leaching also had a certain erosion phenomenon, but the layered structure of the clay minerals was relatively complete. Meanwhile, fine particles were observed adsorbed on the edge of the crystalline layer structure of the clay minerals [36], which prevented the water molecules from entering the interlayer of the clay minerals, reducing the swelling of the clay minerals. Therefore, ammonium acetate had little effect on the swelling, dissolution, and transformation of clay minerals during the rare earth leaching process.

#### 4. Conclusions

The effects of ammonium leaching agents on the rare earth leaching process of weathered crust elution-deposited rare earth ore were studied in this paper. The results indicated that the rare earth leaching efficiencies followed the order ammonium acetate > ammonium chloride > ammonium sulfate, with values of 90.60%, 85.96%, and 84.12%, respectively. The swelling ratios of clay minerals followed the order ammonium acetate < ammonium chloride < ammonium sulfate, with values of 2.09%, 2.50%, and 2.89%, respectively. As seen from the thermogravimetric analysis of ore samples, the interlayer adsorbed water contents were 1.29% and 1.41% when the ammonium chloride and ammonium sulfate were used as leaching agents. Meanwhile, the interlaminar water was only 0.85% when ammonium acetate was used as the leaching agent. The action of the leaching agent also leads to the interconversion of clay minerals. The clay minerals were transformed mainly from illite to montmorillonite and kaolinite under the action of the three leaching agents. When ammonium acetate was used as the leaching agent, the relative conversion of illite was 1.49% and that of smectite was only 0.17%. SEM analysis showed that the clay minerals expanded and dissolved obviously when ammonium chloride and ammonium sulfate were used as leaching agents. Meanwhile, the clay mineral layered structure was relatively complete when ammonium acetate was used as the leaching agent. Therefore, ammonium acetate as a leaching agent had the least influence on the swelling, dissolution, and transformation of clay minerals.

It is important to realize the safe and efficient recovery of rare earth in the leaching process of weathered crust elution-deposited rare earth ore. In rare earth leaching, the expansion, dissolution, and transformation of clay minerals by leaching agents represent a safety problem that cannot be ignored. It is worth studying this to reduce the safety risks of mine production by adding green and efficient leaching agents. The results of this paper are beneficial to the selection of rare earth leaching agents and have significance for the efficient utilization of rare earth resources.

**Author Contributions:** Z.Z. and R.C. conceived and designed the experiments; W.C. and C.Z. performed the experiments; F.L. and Z.C. analyzed the data; R.C. and Z.Z. supplied the reagents/materials/analysis tools; W.C. and Z.Z. wrote the paper. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Nature Science Foundation of China (92162109, 52222405 and 52074195) and the Graduate Innovative Fund of Wuhan Institute of Technology (CX2022570).

**Data Availability Statement:** The original contributions presented in the study are included in the article; any further inquiries can be directed to the corresponding authors.

**Acknowledgments:** Thank you to the editors and reviewers for the great effort.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Wang, D.H. Study on critical mineral resources: Significance of research, determination of types, attributes of resources, progress of prospecting, problems of utilization, and direction of exploitation. *Acta Geol. Sinica* **2019**, *93*, 1189–1209. [\[CrossRef\]](#)
2. Zhang, Z.Y.; He, Z.Y.; Xu, Z.G.; Yu, J.X.; Zhang, Y.F.; Chi, R.A. Rare earth partitioning characteristics of China rare earth ore. *J. Rare Earths* **2016**, *37*, 121–127. [\[CrossRef\]](#)
3. Chen, W.D.; Zhang, Z.Y.; Long, F.; Chen, Z.; Chi, R.A. Rare earth occurrence states of weathered crust elution-deposited rare earth ores in southern Yunnan. *Minerals* **2023**, *13*, 554. [\[CrossRef\]](#)
4. Lu, L.; Liu, Y.; Liu, H.C.; Zhao, Z.; Wang, C.H.; Xu, X.C. geochemical and geochronological constraints on the genesis of ion-adsorption-type REE mineralization in the Lincang Pluton, SW China. *Minerals* **2020**, *10*, 1116. [\[CrossRef\]](#)
5. Zhu, X.P.; Zhang, B.; Ma, G.T.; Pan, Z.W.; Hu, Z.G.; Zhang, B.T. Mineralization of ion-adsorption type rare earth deposits in Western Yunnan, China. *Ore Geol. Rev.* **2022**, *148*, 104984. [\[CrossRef\]](#)
6. Feng, Y.Z.; Chen, H.Y.; Xiao, B.; Chu, G.B.; Zheng, H.; Shen, C. REE remobilization of allanite: Implications for the formation of ion-adsorption REE deposits, South China. *Chin. Sci. Bull.* **2023**, *68*, 1217–1229. [\[CrossRef\]](#)
7. Zhang, Z.Y.; He, Z.Y.; Yu, J.X.; Xu, Z.G.; Chi, R.A. Novel solution injection technology for in-situ leaching of weathered crust elution-deposited rare earth ores. *Hydrometallurgy* **2016**, *164*, 248–256. [\[CrossRef\]](#)
8. Zhang, M.; Tan, W.; He, X.C.; Zhao, F.F.; Luo, L.Y. Analysis on geological characteristics and discussion about metallogenic process for ion-adsorption type REE deposit in Lancang County, Yunnan Province. *Miner. Depos.* **2022**, *41*, 567–584. [\[CrossRef\]](#)
9. Zhang, Z.Y.; Chi, R.A.; Chen, Z.; Chen, W.D. Effects of ion characteristics on the leaching of weathered crust elution-deposited rare earth ore. *Front. Chem.* **2020**, *8*, 605968. [\[CrossRef\]](#)
10. Chi, R.A.; Tian, J.; Luo, X.P.; He, Z.Y. The basic research on the weathered crust elution-deposited rare earth ores. *Nonferrous Met. Sci. Eng.* **2012**, *3*, 1–13. [\[CrossRef\]](#)
11. Zhang, Z.Y.; Li, H.; Chi, R.A.; Long, F.; Chi, X.W.; Chen, W.D.; Chen, Z. Inhibition on the swelling of clay minerals in the leaching process of weathered crust elution-deposited rare earth ores. *Appl. Clay Sci.* **2022**, *216*, 106362. [\[CrossRef\]](#)
12. Zhao, L.S.; Huang, X.W.; Feng, Z.Y.; Liu, D.P.; Zheng, X.D.; Yin, W.Q. Research progresses and development tendency of pollution prevention and control technologies for mining of weathered crust elution-deposited rare earth ore. *J. Chin. Soc. Rare Earths* **2022**, *40*, 988–997. [\[CrossRef\]](#)
13. Yin, S.H.; Chen, X.; Yan, R.F.; Wang, L.M. Pore structure characterization of undisturbed weathered crust elution-deposited rare earth ore based on X-ray Micro-CT scanning. *Minerals* **2021**, *11*, 236. [\[CrossRef\]](#)
14. Chi, R.A.; Liu, X.M. Prospect and development of weathered crust elution-deposited rare earth ore. *J. Chin. Soc. Rare Earths* **2019**, *37*, 129–140.
15. Chi, R.A.; Zhang, Z.Y.; Yu, J.X.; Xiao, C.Q.; Zhang, Y.F.; Zhou, F.; Liu, D.F.; Wu, X.Y. Research process of weathered crust elution-deposited rare earth ore. *J. China Univ. Min. Technol.* **2022**, *51*, 1178–1192. [\[CrossRef\]](#)
16. Luo, J.K. Progress in extraction technology for weathered crust elution-deposited rare earth ore. *Met. Ore Dress. Abroad* **1993**, *12*, 19–28.
17. Zhou, J.M.; Li, M.Y.; Yuan, P.; Li, Y.; Liu, H.M.; Fan, W.X.; Liu, D.; Zhang, H. Partial rehydration of tubular halloysite (7 Å) immersed in La(NO<sub>3</sub>)<sub>3</sub> solution for 3 years and its implication for understanding REE occurrence in weathered crust elution-deposited rare earth ores. *Appl. Clay Sci.* **2021**, *213*, 106244. [\[CrossRef\]](#)
18. Huang, Y.F.; He, H.P.; Liang, X.L.; Bao, Z.W.; Tan, W.; Ma, L.Y.; Zhu, J.X.; Huang, J.; Wang, H. Characteristics and genesis of ion adsorption type REE deposits in the weathering crusts of metamorphic rocks in Ningdu, Ganzhou, China. *Ore Geol. Rev.* **2021**, *135*, 104173. [\[CrossRef\]](#)
19. Chen, Z.; Zhang, Z.Y.; Liu, D.F.; Chi, X.W.; Chen, W.D.; Chi, R.A. Swelling of clay minerals during the leaching process of weathered crust elution-deposited rare earth ores by magnesium salts. *Powder Technol.* **2020**, *367*, 889–900. [\[CrossRef\]](#)
20. He, Z.Y.; Zhang, R.; Sha, A.Y.; Zuo, Q.; Xu, Z.G.; Wu, M.; Chi, R.A. Anti-swelling mechanism of DMDACC on weathered crust elution-deposited rare earth ore. *J. Rare Earths* **2022**, *40*, 1803–1811. [\[CrossRef\]](#)
21. Liu, E.H.; Huang, J.; Tan, W.; Liang, X.L.; Ma, L.Y. Constraints on the REE enrichment-fractionation in weathering crust by the mineral evolution in the weathering and leaching processes: A case study of the Renju REE deposit in the Meizhou area, Guangdong, China. *Bull. Miner. Petrol. Geochem.* **2022**, *41*, 464, 517–526. [\[CrossRef\]](#)
22. Jin, X.W. Study on Migration and Transformation of Clay Minerals in Ionic Rare Earth Ore under Leaching Conditions. Master's Thesis, Jiangxi University of Technology, Nanchang, China, 2021; p. 45. [\[CrossRef\]](#)
23. Wang, L.; Liao, C.F.; Yang, Y.M.; Xu, H.B.; Xiao, Y.F.; Yan, C.H. Effects of organic acids on the leaching process of ion-adsorption type rare earth ore. *J. Rare Earths* **2017**, *35*, 1233–1238. [\[CrossRef\]](#)
24. Chen, W.D.; Zhang, Z.Y.; Chi, R.A. Assisted leaching process of weathered crust elution-deposited rare earth ore by ammonium carboxylate. *Met. Mines* **2020**, *5*, 191–196. [\[CrossRef\]](#)

25. Xu, R.H.; Wang, R.J.; Xiao, W.S.; Dong, L.S.; Liu, Y.G. Variations in clay mineral composition in the western Arctic Ocean since the mid-Pleistocene: Implications on changes in circulation and ice sheet development. *Acta Oceanol. Sin.* **2020**, *42*, 50–60.
26. Lin, Z.X. Distinguishing Halloysite from Kaolinite by the Use of Dimethyl Sulfoxide Treatment. *Rock Miner. Anal.* **1988**, *1*, 58–61.
27. Zhang, Z.Y.; Wang, G.S.; Li, C.H.; Chi, R.A.; Long, F.; Chen, Z.; Chi, X.W.; Liu, D.F. Application of chromatographic plate theory on the weathered crust elution-deposited rare earth ore with carboxylate. *Physicochem. Probl. Miner. Process.* **2021**, *57*, 48–62. [[CrossRef](#)]
28. Li, F.C.; Li, S.; Yang, Y.Z.; Cheng, L.J. Advances in the study of weathering products of primary silicate minerals exemplified by mica and feldspar. *Acta Petrol. Mineral.* **2006**, *5*, 440–448.
29. Xiao, Y.F.; Gao, G.H.; Huang, L.; Feng, Z.Y.; Lai, F.G.; Long, Z.Q. A discussion on the leaching process of the ion-adsorption type rare earth ore with the electrical double layer model. *Miner. Eng.* **2018**, *120*, 35–43. [[CrossRef](#)]
30. Liu, Z.; Zhang, Z.Y. Study on the mechanism of ammonium acetate inhibiting the swelling of clay minerals in weathering crust eluvial rare earth ores. *Ind. Miner. Process.* **2019**, *4*, 33–37, 42. [[CrossRef](#)]
31. Chen, K.H. Morphology of the crystals of kaolinite halloysite minerals and its evolution. *Sci. Geol. Sin.* **1981**, *1*, 30–38, 97, 98.
32. Lin, C.X.; Zheng, Z.P. Experimental studies on metallogenetic mechanism of weathering crust-leaching REE deposits in southern China. *Geochimica* **1994**, *2*, 189–198. [[CrossRef](#)]
33. Wang, Q.; Ma, L.; Huang, K.J.; Lei, Z.Y.; Xie, S.Y. Quantitative analysis of kaolinite, illite and montmorillonite by X-ray diffraction. *Guizhou Geol.* **2021**, *38*, 71–78.
34. Chen, T.; Wang, H.J.; Zhang, Z.Q.; Wang, H. An approach to paleoclimate-reconstruction by clay minerals. *Acta Sci. Nat. Univ. Pekin.* **2005**, *2*, 309–316. [[CrossRef](#)]
35. Luo, G.X.; Yi, C.; Zhang, Z.L.; Zhang, Y.; Hu, L.F. Features of clay minerals in the sandstones of middle Jurassic Yan'an Formation of Bayinqingeli-Suhaitu area, northern Ordos Basin. *World Nucl. Geosci.* **2021**, *38*, 162–173.
36. Liu, Z. Study on the Mechanism of Inhibition of Swelling and Inhibition of Aluminum in Leaching Rare Earth Minerals from Weathered Crust Elution-Deposited Rare Earth Ore by Carboxylic Ammonium Salt. Master's Thesis, Wuhan Institute of Technology, Wuhan, China, 2019. [[CrossRef](#)]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.