Characteristics and Influencing Factors of the Granite Weathering Profile: A Case Study of a High Latitude Area in Northeastern China

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Abstract: Rock weathering, an important geological process on the earth’s surface, plays a key role in shaping surface morphology, providing nutrients needed by the ecosystem, and regulating the global climate. However, the regimes for controlling rock weathering in different regions are still controversial. In this respect, the heavy minerals, elements, Sr-Nd isotope, magnetic susceptibility, and chromaticity of the granite weathering profile in Harbin, a high latitude area of China, were analyzed for understanding the weathering characteristics and mechanisms of the granite weathering profile in the cold area. The results indicate that the profile underwent strengthened physical weathering (large volumes of cracks in the granite parent rock) and low–moderate chemical weathering (CIA = 56~68). However, the chemical weathering does not clearly affect the composition of the weathering products, making the weathering products a good inheritance from the parent rocks, as evidenced by the binary diagram (e.g., TiO$_2$-Zr, and La/Sc-Co/Th) and geochemical genes (LG01 and LG03). The development process of the weathering profile has been affected by the input of external materials and biological activities, as evidenced by the Sr-Nd isotopic composition, Th/Zr values, chemical depletion fractions, $\Delta$Al/Ti ratios, $\chi_{fd}$%, and geochemical genes (LG03). Notably, a progressively decreasing weathering degree with a reduced depth is observed in the profile, which is likely to be related to an addition of external materials and/or effects of biological activities. In addition, the weathering regime of the profile does not vary in geology time, characterized by a kinetic-limited weathering regime with a limited supply.

Keywords: granite weathering profile; heavy minerals; Sr-Nd isotope composition; geochemical gene; geochemistry; kinetic-limited weathering

1. Introduction

As an important geological process of the earth’s surface, rock weathering plays a key role in shaping the surface morphology, providing nutrients needed by the ecosystem, and regulating the global climate [1]. Silicate weathering is an important link in the global CO$_2$ source-sink processes and is considered to be the record of the interaction and long-term changes of the critical zone [2,3]. The weathering profiles of rocks are continuous and provide a long-term record of both the regional environment’s evolution and the elements’ geochemical cycles [4]. Previous scholars have carried out a large amount of research on the weathering mechanism, element migration, and environmental control factors of silicate weathering processes at a profile scale, mainly focusing on basalt [5–9] and granite [10–22]. Among them, the widely distributed granite, accounting for 1/4 of the surface’s exposed rocks, is an important research object [23–25]. Studying the chemical weathering processes...
of granite through the weathering profile has become an important way to explore the continental weathering and the biogeochemical cycle of elements [26–30].

Rock weathering is usually controlled by a variety of factors, such as climate, tectonic movement, topography, and biological activity, but the importance of each factor varies across geographic regions [4,25,31–38]. Two end-members in the framework of chemical weathering rate limitations, supply-limited and kinetic-limited weathering, can be used to assess the response of weathering to the environment [1,24,39,40]. In supply-limited weathering processes, weathering rates are closely related to mineral supply rates [31,41], and strong tectonic activities produce a large number of fractures and rock debris, which can intensify rock decomposition and the supply of fresh minerals [42–44]. In kinetic-limited weathering processes, most studies attribute the degree of rock weathering to climatic factors [1,31,45,46]. The change in weathering environment can change the degree of the physical and chemical weathering of rocks [24,31,37,40,47]. Physical weathering decomposes the rock through expansion and contraction, frost wedging, salt crystallization, and deliquation [48], and does not affect the rock’s mineral and elemental composition. Chemical weathering can affect the distribution of elements through the complexation of organic and inorganic matter [27,28,49,50], and also transforms primary minerals into secondary minerals [51,52]. In addition to physical and chemical weathering, biological activities and their metabolites can have an impact on rock weathering through the secretion of organic acids and the behavior of specific elements.

The controlling factors of rock weathering can be revealed by studying the geochemical behavior of elements and mineral assemblages [53]. Among them, the mass transfer coefficient is widely used in the study of element behavior [54–61]. Studying the migration and enrichment degree of major and trace elements in weathering products relative to the parent rock can reveal the influence of weathering on element behavior. The migration and enrichment behavior of rare earth elements plays an important role in the study of element geochemistry and has been widely studied [62–72]. The content of rare earth elements in the granite weathering profile is mainly controlled by the parent rock, and the variation depends on the difference in the weathering resistance of minerals containing rare earth elements [73]. Light rare earth elements are mainly found in monazite, and heavy rare earth elements are mainly found in apatite and zircon [74]. The weathering resistance of different minerals is different, inducing the different contents of light and heavy rare earth elements in a weathering profile, and thus the influencing factors of the rock weathering process can be revealed according to the behavior of rare earth elements.

Heavy minerals are stable and resistant to weathering and abrasion among rock-forming minerals. In the process of weathering, the changes in heavy mineral assemblages are only affected by the weathering degree of the parent rock and are not interfered with by foreign substances [75]. Therefore, the influencing factors of rock weathering can also be inferred from the characteristics of heavy mineral assemblages in the weathering profile. Isotopic geochemistry is widely used to trace various biogeochemical processes on a global scale [76,77]. Among them, the Sr isotope is considered to be the main tracer because of its activity in the chemical weathering process and its easy removal from weathering profiles [78]. The Nd element has low solubility in water and is not affected by transport and diagenetic processes [79], so the $^{143}\text{Nd} / ^{144}\text{Nd}$ ratio is a reliable indicator of geochemical processes, which can provide powerful constraints for regional weathering environment evolution [80,81]. The geochemical gene is an elemental geochemical tracing method that has been proposed in recent years [82–84]. The elemental content is arranged in a certain order according to the difference in the elemental composition of different rocks, and on this basis, the elemental content is assigned a code (0, 1, 2) in the order of rising, flat, or falling. By calculating the similarity of genes between the parent rock and weathering products, the inheritance of the weathering products relative to the parent rock can be determined [82–84].

In previous studies, the element ratio and clay mineral composition were used to judge the factors affecting granite weathering, but there were no other effective geological
means. In addition, most of the previous research objects are mainly granite weathering profiles of subtropical and tropical areas [70,85–90], and there is little research on the granite weathering profiles of high latitudes [91]. In this study, the weathering profile of the granite in the Harbin Yingjie area is selected for understanding the weathering characteristics of the high-latitude area of NE China through a combination of mineralogy, geochemistry, magnetic susceptibility, and chromaticity. More importantly, the possible influencing factors of the weathering process are discussed, and the weathering mechanism is further explored. The present study provides a new research idea for explaining the weathering characteristics and mechanisms of the granite weathering profile of cold areas.

2. Materials and Methods

2.1. Regional Setting

The research area is located in the southeastern portion of the Songnen Massif and the west side of the Zhangguangcai Range (Figure 1). The Songnen Massif was formed by the collision of the paleoasian ocean plate and ancient continental plate in the Precambrian [92]. In the late Early Paleozoic, the Songnen Massif and the Jiamusi Massif amalgamated along the fault zone [93–95]. In the Palaeozoic and Mesozoic, a large number of granites occurred in the southeastern part of Harbin due to the subduction, collision, and amalgamation of the micro-blocks [93,94,96–100]. The Zhangguangcai Range, located in the eastern part of the Songnen Massif, was influenced by the tectonic evolution of the paleoasian ocean plate and the ancient continental plate in the Precambrian, forming a large area of granite [101,102].

Harbin has a typical mid-temperate continental monsoon climate, with large diurnal and annual temperature ranges and dramatic variations in hot and cold. The East Asian summer monsoon (EASM) from the North Pacific results in low and uneven summer precipitation in the study area due to a block of the eastern mountains. Additionally, the cold and dry air flow brought by the East Asian winter monsoon (EAWM) and the high-latitude position of the region lead to the unusually cold climate in winter in the region.

Figure 1. (a) DEM map of East Asia; (b) Granite distribution map of NE China, modified from Chen et al. [93]; (c) Geological map of study area, modified from 1:500,000 geological map of Heilongjiang Province.
2.2. Weathering Profile Description and Sampling

The studied granite weathering profile is located in Yingjie Village, Binxian County, Harbin City, Heilongjiang Province, China (127°20′49″ N, 45°42′50″ E), with a depth of about 3.6 m. According to the lithologic characteristics of the Yingjie granite weathering profile, it can be divided into three distinct weathering layers from top to bottom (Figure 2):

![Figure 2. (a) Outcrop photograph of the investigated regolith profile. (b) Sample position and layers in the profile. The profile is divided into three parts, from top to bottom, consisting of oxidized soil, saprolite, and semi-weathered layers.](image)

- An oxidized soil layer (A layer, 0–120 cm): The upper layer is of an 85 cm thick greyish-white to yellowish-white oxidized soil, with some small rock debris (commonly <2 cm); 85–120 cm is a grayish-yellow transition layer with a hard texture.
- A saprolite layer (B layer, 120–280 cm): This layer is made up of purple-red mud formed by granite weathering, and its upper part is delicate with a loose texture; from 160 cm, the grain size of the sediments gradually increases with increasing depth and the weathering along the joints is obvious; from 239 cm, it is purplish-red and muddy with fine and small rock debris.
- A semi-weathered layer (C layer, 280–350 cm): This layer is made up of purplish-red mud with large rock debris, containing fine joints, and the bottom gradually transfers into the granite bedrock.

The upper layer of the profile developed a black soil which was covered with vegetation and crops. In order to avoid the possible anthropogenic influence, we did not sample the top 30 cm-thick black soil layer. Twenty-five samples were collected at an interval of 10 cm along the weathering profile, successively named YJ-1–YJ-25. Meanwhile, in order to compare before and after weathering, two fresh granite parent rocks (YJ-26) were collected near this section.

2.3. Laboratory Analysis
2.3.1. Element Geochemistry

In order to eliminate the interference of grain size on minerals, the granite weathering samples were screened into <63 µm fraction for geochemical analysis. An inductively coupled plasma optical emission spectrometry (ICP-OES) was used to analyze the major elements. Two kinds of pretreatment methods were used in this study. The Si content was analyzed via the alkali-fusion method to exclude the influence of Na⁺ on Si content in the sample, and other major elements were analyzed via the acid-leading method, which has the advantages of a more thorough extraction and smaller error [103]. Trace and rare earth elements were determined by Inductively coupled plasma-Mass Spectrometry (ICP-MS). The relative standard deviation of the major elements is 0.01%, and the trace elements’
and rare earth elements’ are 0.01–0.05 ppm. The analysis of element geochemistry was completed in the Key Laboratory of Mineral Resources in Western China (Gansu Province), Lanzhou University.

2.3.2. Heavy Mineral Identification

Before the identification of heavy minerals, the samples were screened after drying, and the fractions with a size of >63 µm were retained for the separation of heavy minerals from light minerals using tribromomethane. The separated samples were repeatedly rinsed with alcohol until clean, and then put into a drying oven at 60 °C for drying. The dried samples were subjected to strong magnetic separation (accuracy < 0.1 mg) and weighed again after obtaining the non-magnetic, electromagnetic, and strong magnetic minerals. A stereo-binocular microscope was used to observe and identify the separated heavy minerals, and the number of the identified heavy mineral particles for each sample was controlled to be more than 1000. The mass percentage of heavy minerals was used in this study. The heavy mineral identification was completed at the Langfang Chengxin Geology Company (Langfang, China).

2.3.3. Sr-Nd Isotope Analysis

To eliminate the influence of secondary carbonates on Sr isotopic composition, <63 µm fractions were screened from the bulk samples and soaked in a 0.5 mol/L acetic acid solution for 4 h to obtain an acid-insoluble substance, and then dried. The Sr and Nd were separated via the standard ion exchange method, and the Sr and Nd isotopic ratios were normalized with $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, respectively, to correct the mass fractionation effect. The analytical blank was <1 ng for Sr and <50 pg for Nd. The Nd isotopic composition is expressed by the εNd (0) value, normalized by the modern value of the chondrite homogeneous source of $^{143}\text{Nd}/^{144}\text{Nd} = 0.512638$. The determination of the Sr and Nd isotope was completed in the Key Laboratory of Mineral Resources in Western China (Gansu Province), Lanzhou University.

2.3.4. Magnetic Susceptibility Test

Samples for magnetic susceptibility analysis were first crushed and then powdered to 200 mesh with an agate mortar. The ground samples were placed in a weak magnetic box (2 × 2 × 2 cm), and the high-frequency magnetic susceptibility ($\chi_{hf}$) and low-frequency magnetic susceptibility ($\chi_{lf}$) were measured after being weighed, respectively, using a Bartington MS2B susceptibility meter operated at dual frequency. Each sample was tested three times to ensure its accuracy and the average value was calculated as the mass susceptibility value for the final test. The magnetic susceptibility test was completed in the Heilongjiang Province Key Laboratory of Geographical Environment Monitoring and Spatial Information Service in Cold Regions, Harbin Normal University.

2.3.5. Chromaticity Analysis

The dried samples were ground to pass through a 200-mesh sieve and then placed on a glass sheet. In order to avoid the existence of accidental experimental results resulting in errors, the luminance ($L^*$), redness ($a^*$), and yellowness ($b^*$) of the samples were measured three times by the Minolta CM-700d spectrophotometer and the average values were obtained. The chromaticity analysis was completed in the Heilongjiang Province Key Laboratory of Geographical Environment Monitoring and Spatial Information Service in Cold Regions, Harbin Normal University.

2.3.6. Loss on Ignition Test

After drying, the samples were placed into the weighed crucible (error not more than 0.01 g) and the net weight ($m_1$) was recorded before burning. Then the samples were put in a Muffle furnace and burned at 1000 °C for one hour, weighed again ($m_2$) after being
cooled to room temperature. The LOI test was completed in the Key Laboratory of Mineral Resources in Western China (Gansu Province), Lanzhou University.

2.4. Mathematical Calculation

2.4.1. Calculation of Chemical Weathering Index

The chemical weathering process is mainly accompanied by the loss of mobile elements and the enrichment of immobile elements in silicate minerals. Therefore, the ratios of mobile to immobile elements are frequently used to quantitatively evaluate the chemical weathering degree. A CIA is a considerably effective index for the assessment of the degree of rock chemical weathering and the reconstruction of the weathering environment [104]. The calculation formula is as follows:

\[
\text{CIA} = \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}) \times 100}
\]

(1)

The element content is expressed in molar ratio, and CaO* only represents the Ca content in silicate minerals, which is usually calculated as CaO* = \(\min (\text{CaO} - \frac{10}{3} \times \text{P}_2\text{O}_5, \text{Na}_2\text{O})\).

In order to avoid the influence of potassium metasomatism in the weathering process, a chemical weathering index (CIW) was introduced to calculate the degree of granite weathering [105]. The calculation formula is as follows:

\[
\text{CIW} = \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O}) \times 100}
\]

(2)

In addition to the above indexes, this paper also further calculated the weathering degree of the granite weathering profile by using the Weathering Index of Colman (WIC): \([\{(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO}^* + \text{MgO})/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{TiO}_2)\] \times 100\) [106], the granite weathering index (WIG): \([\{(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO}-10/3\text{P}_2\text{O}_5)/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{TiO}_2)\] \times 100\) [107], and the Plagioclase index of alteration (PIA): \((\text{Al}_2\text{O}_3 \times \text{K}_2\text{O})/(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} \times \text{K}_2\text{O}) \times 100\) [108].

Considering that the volume of rocks changes during weathering, the chemical depletion fraction (CDF) is used to represent the mass loss fraction of weathering materials relative to unweathered bedrock [59]. The calculation formula is as follows:

\[
\text{CDF} = (1 - \frac{[X_i]_{\text{rock}}}{[X_i]_{\text{saprolite}}})
\]

(3)

where \([X_i]_{\text{rock}}\) and \([X_i]_{\text{saprolite}}\) are the concentrations of an immobile element in rock and saprolite, respectively. When CDF = 0, there is no loss of soluble elements in the weathering samples compared with the parent rock; CDF > 0 represents the total mass loss of elements during weathering. The CDF value does not exceed 0.5 because a large proportion of the primary Si is fixed in insoluble quartz and large amounts of Si, Fe, and Al released from the original mineral are retained in the clay minerals, so the CDF value is often considered a reliable indicator of chemical weathering [109–111].

2.4.2. Mass Transfer Calculations

In order to evaluate the behavior of elements during chemical weathering, the mass transfer coefficient \((\tau)\) is applied to calculate the changes in element composition in the whole weathering profile relative to the parent rock [112,113], as follows:

\[
\tau_X = \frac{[X_i]_{\text{weathered}}/[X_i]_{\text{parent}}}{([X_i]_{\text{weathered}}/[X_i]_{\text{parent}}) - 1}
\]

(4)

where \([X_i]_{\text{weathered}}\) and \([X_i]_{\text{parent}}\) represent the concentration of element X in the weathering sediments and parent rock, respectively; \([X_i]_{\text{weathered}}\) and \([X_i]_{\text{parent}}\) are the concentrations of the immobile element. When \(\tau = 0\), the concentration of the X element in the weathered sample has no loss compared with that in the parent rock; When \(\tau < 0\), it means that elements have been lost in the weathering process; When \(\tau > 0\), it means that elements are enriched relative to the parent rock during weathering; \(\tau = -1\) indicates that elements completely disappear during weathering.
2.4.3. Ce and Eu Anomaly Calculation

During the diagenesis and weathering of rocks, Ce and Eu elements behave differently from other rare earth elements either through fractionation between elements or through their own oxidation changes. Therefore, the anomalies of Ce and Eu elements after chondrite normalization can provide valuable weathering information [114,115]. Ce and Eu anomalies are obtained through the linear interpolation of adjacent elements [116,117]:

\[
\delta \text{Ce}_N = 2 \times \frac{\text{Ce}_N}{(\text{La}_N + \text{Pr}_N)} \\
\delta \text{Eu}_N = 2 \times \frac{\text{Eu}_N}{(\text{Sm}_N + \text{Gd}_N)}
\]

where Ce\textsubscript{N}, La\textsubscript{N}, Pr\textsubscript{N}, Eu\textsubscript{N}, Sm\textsubscript{N}, and Gd\textsubscript{N} are the elemental concentrations normalized to the chondrites. \( \delta \text{Ce}_N \) and \( \delta \text{Eu}_N \) > 1 are positive anomalies and < 1 is a negative anomaly.

2.4.4. Calculation of Chromaticity and Frequency-Dependent Susceptibility

In order to quantitatively describe the coloring degree of the samples, we defined the color strength index (CSI), which indicates the distance from the origin to the \( a^* \) and \( b^* \) value on the coordinate system, and was calculated as follows:

\[
\text{CSI} = \sqrt{(a^*)^2 + (b^*)^2}
\]

In order to further verify the change of magnetic susceptibility in the process of granite weathering, the frequency-dependent susceptibility (\( \chi_{fd\%} \)) of the weathering samples was calculated as follows:

\[
\chi_{fd\%} = \frac{(\chi_{lf} - \chi_{hf})}{\chi_{lf}} \times 100
\]

3. Results

3.1. Granite Parent Rock

The fresh surface of the unweathered granite sample (YJ-26) is gray-white in color, with a medium-to-coarse-grained granitic structure and massive structure, composed of quartz, potassium feldspar, plagioclase, and mica.

The geochemical analysis results of the granitic parent rock show that the proportions of SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, Na\textsubscript{2}O, and K\textsubscript{2}O are high, of which the SiO\textsubscript{2} content is the highest, up to 67%, followed by Al\textsubscript{2}O\textsubscript{3} (18.3%); the contents of Na\textsubscript{2}O and K\textsubscript{2}O are similar, at 5.8% and 5.4%, respectively. The A/NK-A/CNK diagram shows that the aluminum saturation index A/CNK of the parent rock is 1.58 (Supplementary Figure S1a), indicating that the granite has the characteristics of peraluminous granite; in the diagram of SiO\textsubscript{2}-K\textsubscript{2}O, the characteristics of the high potassium calcium for the granitic parent rock are shown (Supplementary Figure S1b). The \(^{87}\text{Sr}/^{86}\text{Sr} \) of the granite parent rock is 0.7250159 (Supplementary Table S1), combined with the geochemical characteristics of the parent rock (low Na/K ratio, high rare earth concentration, A/CNK > 1.1), and thus, we make a detection of the S-type granite [118,119]. In the granite parent rock, the contents of large ion lithophile elements (LILEs), high field strength elements (HFSEs), and rare earth elements (REEs) are relatively high. The results of the chondrite standardization of rare earth elements show a negative Eu anomaly and a slight positive Ce anomaly.

The heavy mineral composition in the granite parent rock is shown in Table 1. The heavy minerals are mainly hematite-limonite and zircon, which account for 89.51% and 3.15%, respectively. In addition, there are also a small amounts of anatase (0.64%), magnetite (0.59%), leucoxene (0.01%), and pyroxene (0.15%). The observation shows iron-stained felsic rock-forming minerals in the granite parent rock.
Table 1. The heavy mineral composition (%) of the granite weathering products and granite parent rock. "/" indicates that the heavy mineral is not observed, and "△" indicates that the heavy mineral is an occasional mineral with a number < 3. Others refer to weathered debris produced during the weathering of rocks.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Zircon</th>
<th>Leucoxene</th>
<th>Rutile</th>
<th>Anatase</th>
<th>Epidote</th>
<th>Pyroxene</th>
<th>Hematite-Limonite</th>
<th>Magnetite</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>YJ-2</td>
<td>0.68</td>
<td>0.00</td>
<td>0.00</td>
<td>0.03</td>
<td>0.56</td>
<td>/</td>
<td>81.82</td>
<td>14.28</td>
<td>2.63</td>
</tr>
<tr>
<td>YJ-5</td>
<td>1.93</td>
<td>0.01</td>
<td>/</td>
<td>0.15</td>
<td>△</td>
<td>/</td>
<td>91.76</td>
<td>0.60</td>
<td>5.55</td>
</tr>
<tr>
<td>YJ-8</td>
<td>1.74</td>
<td>0.16</td>
<td>/</td>
<td>2.19</td>
<td>△</td>
<td>/</td>
<td>88.50</td>
<td>/</td>
<td>7.42</td>
</tr>
<tr>
<td>YJ-13</td>
<td>0.35</td>
<td>0.02</td>
<td>/</td>
<td>0.70</td>
<td>△</td>
<td>/</td>
<td>90.60</td>
<td>/</td>
<td>8.33</td>
</tr>
<tr>
<td>YJ-17</td>
<td>0.67</td>
<td>0.01</td>
<td>/</td>
<td>0.81</td>
<td>△</td>
<td>/</td>
<td>89.63</td>
<td>/</td>
<td>8.87</td>
</tr>
<tr>
<td>YJ-21</td>
<td>0.64</td>
<td>0.00</td>
<td>/</td>
<td>0.82</td>
<td>△</td>
<td>△</td>
<td>92.47</td>
<td>/</td>
<td>6.07</td>
</tr>
<tr>
<td>YJ-26</td>
<td>3.16</td>
<td>0.01</td>
<td>/</td>
<td>0.64</td>
<td>△</td>
<td>△</td>
<td>89.51</td>
<td>0.59</td>
<td>5.94</td>
</tr>
</tbody>
</table>

3.2. Heavy Minerals and Geochemistry of Weathering Profile

3.2.1. Major Elements

The SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ contents are relatively high in the weathering profile. Specifically, the content of SiO$_2$ is the highest (59.2%~72%) with a decreasing tendency toward increasing depth, followed by Al$_2$O$_3$ (14.7%~23.2%) and Fe$_2$O$_3$ (3.8%~7.7%). However, the variation trend of the Al$_2$O$_3$ and Fe$_2$O$_3$ is opposite to that of the SiO$_2$, showing an increasing trend as a whole. Among the alkali metal elements, the contents of Na$_2$O and K$_2$O are higher, while CaO and MgO are lower, ranging from 0.2% to 1.2% and showing a similar trend. The content of TiO$_2$ in the profile is relatively small, ranging from 0.2% to 1%. The contents of MnO and P$_2$O$_5$ are small, accounting for only 0.04%~0.12%. In addition, the profile has a high LOI value (3.1%~22.2%) as a whole.

The profile can be divided into three distinct horizons according to the change in the major elements in the weathering profile (Figure 3a), which is consistent with the observed lithological characteristics in the field. The contents of Al$_2$O$_3$, Fe$_2$O$_3$, K$_2$O, and P$_2$O$_5$ are higher in the semi-weathered layer. LOI values are significantly higher, reaching 22.3 at a 349 cm depth. In the saprolite layer, SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, K$_2$O, and Na$_2$O are dominant, but Al$_2$O$_3$ and Fe$_2$O$_3$ contents are significantly decreased compared to those of the semi-regolith layer, and SiO$_2$ contents are increased to a certain extent. The fluctuation of the major elements in the saprolite layer is small. In the oxidized soil layer, the contents of SiO$_2$, CaO, MgO, and TiO$_2$ reach the highest values among the three layers, while the contents of Al$_2$O$_3$, Fe$_2$O$_3$, and K$_2$O are in the lowest values.

3.2.2. Trace and Rare Earth Elements

The variation trend of heavy metals, such as Ni, V, Cr, and Co, with depth is similar to that of Fe$_2$O$_3$ and MnO (Figure 3b). The content of the large ionic lithophile element Rb decreases with depth, which is consistent with K$_2$O. The contents of high-field strength elements Zr, Hf, Nb, Ta, and Th show a high consistency in the profile (Figure 3b).

The weathering profile is enriched in rare earth elements, showing a good inheritance from the parent rocks. However, the total of rare earth elements (ΣREE) varies greatly (231.2~780.8) in the different layers, basically consistent with the lithological characteristics (Figure 4a). The highest ΣREE value (780.8) is found at a 300 cm depth in the semi-weathered layer. The saprolite layer has little fluctuation and a high content of rare earth elements. The ΣREE values in the semi-weathered layer and saprolite layer are higher than those in the parent rock but are low in the oxidized soil layer.

The content of light rare earth elements (LREEs) is relatively high (204.68~708.98) and has a consistent variation trend with the ΣREE (Figure 4b). The content of heavy rare earth elements (HREEs) is relatively low (26.56~75.59), with a relatively high value in the saprolite layer and the highest value at the junction of the saprolite layer and oxidized soil layer (Figure 4c). The LREE/HREE ratio gradually increases with decreasing depth, with
the maximum value found at the top of the saprolite layer. The La\textsubscript{N}/Yb\textsubscript{N} value ranges from six to thirteen (Figure 4e).

The obvious negative Eu anomaly and inapparent Ce anomaly can be observed in the weathered profile (Figure 4), with a δEu value (0.26~0.56) and a δCe value (0.87~1.1). In the Chondrite-normalized rare-earth element patterns (Supplementary Figure S2), each layer shares an identical pattern characterized by a marked V-type profile.

### 3.2.2. Trace and Rare Earth Elements

The variation trend of heavy metals, such as Ni, V, Cr, and Co, with depth is similar to that of Fe\textsubscript{2}O\textsubscript{3} and MnO (Figure 3b). The content of the large ionic lithophile element Rb decreases with depth, which is consistent with K\textsubscript{2}O. The contents of high-field strength elements Zr, Hf, Nb, Ta, and Th show a high consistency in the profile (Figure 3b).

The weathering profile is enriched in rare earth elements, showing a good inheritance from the parent rocks. However, the total of rare earth elements (∑REE) varies greatly (231.2~780.8) in the different layers, basically consistent with the lithological characteristics (Figure 4a). The highest ∑REE value (780.8) is found at a 300 cm depth in the semi-weathered layer. The saprolite layer has little fluctuation and a high content of rare earth elements. The ∑REE values in the semi-weathered layer and saprolite layer are higher than those in the parent rock but low in the oxidized soil layer.

### 3.2.3. Sr-Nd Isotopic Composition

The $^{87}$Sr/$^{86}$Sr values in the weathering profile range from 0.7144717 to 0.7250159 (Supplementary Table S1), which is lower than that of the parent rock, and the $^{143}$Nd/$^{144}$Nd values have few variations, from 0.512538974 to 0.512668272, which is moderately lower than that of the granite parent rock.

### 3.2.4. Heavy Mineral Characteristics

Hematite-limonite is the main heavy mineral in the weathering profile, with few variations (Table 1). Zircon contents are clearly lower than that of the granite parent rock. The unstable mineral amphibole gradually decreases and disappears through the weathering...
process. Magnetite disappears from the weathering profile, but rapidly increases to 14.28% at the top of the weathering profile (YJ-2). Notably, at the top of the profile, the heavy mineral types have changed, with small amounts of epidote, rutile, and other minerals.

3.3. Characteristics of Chromaticity and Magnetic Susceptibility

Chromaticity test results show that the \( a^* \) and \( b^* \) values in the profile have similar variation trends, while the \( L^* \) values present a completely opposite trend (Figure 5a). The \( a^* \) and \( b^* \) values of the semi-weathering layer and saprolite layer are relatively stable, but the \( L^* \) values fluctuate. The magnetic susceptibility values, i.e., the \( \chi_{hf} \), \( \chi_{lf} \), and \( \chi_{fd} \%), change significantly in the profile (Figure 5b).

![Figure 4](image-url)  
Figure 4. The concentration of total rare earth elements (a), the concentration of light rare earth elements (b), the concentration of heavy rare earth elements (c), LREE/HREE (d), \( \text{La}_N/\text{Yb}_N \) (e), \( \text{Ce}/\text{Ce}^* \) (f) and \( \text{Eu}/\text{Eu}^* \) (g) in the weathered profile of Yingjie granite varies with depth. \( \text{Eu}/\text{Eu}^* = 2 \times \text{Eu}_N/(\text{Sm}_N + \text{Gd}_N) \), \( \text{Ce}/\text{Ce}^* = 2 \times \text{Ce}_N/(\text{La}_N + \text{Pr}_N) \).

![Figure 5](image-url)  
Figure 5. Variations in chroma (a) and magnetic susceptibility (b) in the granite weathering profile.

4. Discussion

4.1. Profile Weathering Characteristics

Field observation shows that there are many cracks in the weathering section. The development of cracks indicates that the granite underwent a large degree of physical weathering [120]. The weathered samples contain more iron-stained felsic rock-forming mineral detritals, and the surface of transparent minerals such as zircon also shows an iron-stained phenomenon. The main iron-containing silicate in the granite is mica, as physical
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weathering (such as expansion and contraction, frost wedging, salt crystallization, and deliquation) causes microcracks in the rock. Reddish-brown inclusions (such as goethite), formed by the oxidation of iron-bearing minerals (e.g., mica) along microcracks, adhere to the surface of the remaining minerals [91,121], consequently causing the rocks to appear reddish-brown in color. In addition, Hematite-limonite can also be converted into goethite during hydration, forming red attachments on the mineral surface, which also leads to the reddish-brown color of the rock. The increasing CSI values from the parent rock to the weathering samples also indicate the formation of red or reddish-brown opaque minerals.

The presence of cracks in the rock and the change in the color of the mineral surface indicate that the granite has undergone physical weathering. However, the decomposition and disappearance of some heavy minerals in the weathering profile cannot be explained by mechanical weathering. Therefore, a quantitative evaluation of the chemical weathering degree is needed. The trend and degree of the rock’s/sediments’ chemical weathering can be predicted (Figure 6) according to the element geochemical data presented in the Al₂O₃-(CaO* + Na₂O)-K₂O (A-CN-K) diagram [122]. The results show that the samples are plotted close to the zone III and IV regions in the A-CN-K diagram, indicating a low level of chemical weathering. In addition, the samples show a trend of approaching the K₂O point, suggesting the abnormal input of K during the weathering process. In the diagram of silicate weathering trends (Figure 6), plagioclase is gradually transformed into smectite as the weathering persistently processes. It is generally believed that the transformation of the clay mineral assemblage can indicate the regional weathering type, and the presence of secondary clay minerals such as Smectite and Illite indicates a low degree of regional chemical weathering [123].

The CIA values (56~68) of the profile show an incipient to intermediate degree of chemical weathering [104]. The CIA values in the profile show an obvious three-stage pattern, which is consistent with the element contents and lithologic stratification results in the field (Figure 7). Notably, the CIA values in the semi-weathered layer are significantly higher than those in the other layers, but the oxidized soil layer has the lowest CIA values, indicating a gradually decreasing chemical weathering degree from the bottom up. This observation is also indicated by the other indicators, e.g., the CIW, PIA, WIC, and WIG (Figure 7). In addition, the LOI variations in the profile are also consistent with those of the CIA values. The variations in the LOI values in the granite profile are related to the formation of constitution water and absorption of water in easily weathered minerals such as amphibole or mica, so LOI values can reflect the degree of rock weathering. The LOI values are the highest in the semi-weathered layer, indicating the highest degree of chemical weathering [124,125].

In conclusion, the granite has experienced a combination of physical and chemical weathering during the weathering process, but the chemical weathering process occurs mainly in the initial stage [122]. The highly developed chemical weathering profile cannot develop in the Harbin area because of the intervention of physical weathering before chemical weathering produces highly weathered minerals [120].

4.2. Effect of Chemical Weathering on the Weathering Granite

4.2.1. Property Determination of the Granite Weathering Products

It is generally accepted that the weathering process of rocks/sediments does not change the nature of their parent rocks, so the immobile element ratios are often employed to make a provenance determination and differentiation between the felsic and mafic sources [126–129]. In the TiO₂-Zr binary diagram, the parent rock and the weathered products almost all fall in the felsic igneous rock area (Figure 8), indicating the inheritance of the weathering products from the granite parent rock, as also indicated in the binary diagram of Co/Th-La/Sc.

However, the composition of weathering products cannot be fully characterized only by a single element or element ratio [60,130,131]. In this respect, the geochemical gene of the parent rock and that of its weathering products were constructed to quantitatively
analyze the heritability and inheritance of the weathering materials in the profile from the perspective of genetic similarity.

Figure 6. (a) Clay mineral proportions and vertical zones of an idealized weathering profile developed on intermediate-acid igneous bedrock, modified from [122]. (b) A-CN-K (Al2O3-(CaO + Na2O)-K2O in molecular proportions) ternary diagram for idealized weathering zones. Zone I, which is the most intensely weathered, has abundant kaolinite and gibbsite in neoformed clay minerals, and thus tends to plot close to the A-apex in the A-CN-K diagram. By contrast, Zone IV, immediately above fresh rock, is the least weathered and is characterized by a dearth of neoformed clay minerals (dominated by smectite or vermiculite, if any), and thus plots close to the feldspar (Pl-Kfs) join line in the A-CN-K diagram. The granite weathering profile in this study was most likely in Zones III–IV, and both A-CN-K and CIA values suggest mild chemical weathering conditions in the Yingjie granite weathering profile. Pl: plagioclase, Kfs: K-feldspar, Ka: kaolinite, Gi: Gibbsite, Ill: Illite, Sm: smectite.

The geochemical gene is a method for characterizing rock characteristics based on the elemental abundance data of acidic rock, intermediate rock, and basic rock in China, and the content variation trend of 11 immobile elements during weathering [82–84]. The stability of immobile elements allows weathered rocks to retain the elemental characteristics of their fresh parent rocks, and the trend of content changes between them can be transmitted from parent rocks to weathered products, which is similar to genetic inheritance in biology. The geochemical gene of the sample is constructed by the relative relationship between the adjacent immobile elements arranged in a certain order. The R%, defined as the genetic similarity between the weathering product and the parent rock, is used to determine the extent to which weathering products inherit the parent rock (Supplementary Text S1). It is a newly proposed tracer method in recent years. So far, seven geochemical genes (LG01, LG02, LG03, MGAu, MGW, REEG01, and REEG02) have been constructed, showing good performance in component classification [82–84,132,133], in which the LG01, LG02, and LG03 gene chains have been widely used to determine the composition variability of rock weathering. Yan et al. (2018) first proposed the LG02 geochemical gene and verified the stability of the LG02 lithologic gene through the cycle process of rock weathering to stream sediments [82]. However, the LG02 gene could not distinguish well between basic and intermediate rocks. On this basis, Gong et al. (2020) proposed the LG01 gene and verified it in acidic rocks and their weathering products, and achieved good results [84]. Li et al.
(2021) proposed the LG03 gene according to the stability differences of the LG01 and LG02 geochemical genes, to exclude the influence of biological activities and the addition of foreign substances on material composition [132]. In order to better analyze the change in material composition during granite weathering, two geochemical genes, LG01 and LG03, were selected to construct and test in this study (Supplementary Text S1).

![Figure 7](image-url) - The variations in the indexes characterizing the chemical weathering degree (CIA, CIW, PIA, WIC, WIG and LOI) in the profile.

![Figure 8](image-url) - The binary diagram of the TiO$_2$-Zr and the La/Sc-Co/Th, indicative of the parent rock nature of the weathering products, modified from [131,134].
The genetic chains of the Yingjie granite parent rock and weathering products were calculated according to the coding modes of LG01 and LG03, and the LG01 and LG03 coding and genetic similarity of the granite and its weathering products were constructed (Supplementary Table S2). The genetic similarity between the weathering products and the granite parent rock is shown in Figure 9. The genetic similarity between the Yingjie granite parent rock and Chinese acid rock is 95% and 100%, respectively, indicating that the granite composition in the study area has no significant variation and belongs to acid rock.

In the weathering products, the similarity of the LG01 gene in the semi-weathered layer and the saprolite layer is more than 80%, so it can be considered that the LG01 gene has a good inheritance in the weathering profile. The similarity of the LG03 gene in the weathering samples is almost 100%, which indicates that the LG03 gene has excellent inheritance during granite weathering.

As mentioned above, the granite weathering products have a good granitic parent rock inheritance and are fully able to identify the parent rock nature despite the fact that chemical weathering, to a certain extent, alters the composition of the elements and minerals of the granite weathering products.

4.2.2. Impact of Weathering on the Elemental and Mineral Composition of Granite

The mass transfer coefficient (τ) is applied to calculate the changes in elemental composition in the whole weathered profile relative to the parent rock [112,113]. The elements Zr, Ti, and Nb are often selected as fixed elements in the τ calculation [36,109,135–137] because these elements are concentrated in weathering-resistant minerals and are chemical weathering-independent. Hewawasam et al. (2013) analyzed the relationship between Zr, Ti, and Nb in soil, saprolite, and rock samples [109]. The ratios of Ti/Zr and Nb/Zr in rock samples show a clear weathering enrichment line, which accurately describes the expected relationship between the concentrations of these elements in the regolith if they do not move at all during weathering and if the concentrations of elements are controlled only by weathering. In this study, the Ti/Zr and Nb/Zr ratios of the sample YJ-26 supply a weathering enrichment line. In the Zr-Ti diagram, the weathering samples are roughly distributed above the weathered enrichment line (Supplementary Figure S3), but in the Zr-Nb diagram, part of the weathering samples are located below the weathering enrichment line, indicating a loss of the Nb element during weathering. In addition, the content of Nb in the granite parent rock is very low, so Zr is selected as the fixed element in this study.

The Na element, a mobile element during rock weathering, is usually used to indicate the weathering process of plagioclase in granite. Because Na mainly occurs in weathering-
susceptible minerals (i.e., plagioclase), there is no obvious enrichment in secondary clay minerals and it will not be absorbed by plant growth [23,32,138]. In addition, the weathering of plagioclase is the key to controlling the weathering of granite. In the process of granite weathering, plagioclase is first weathered, consequently producing a large number of cracks and intensifying chemical weathering [23,138,139]. As shown in Figure 10, the mass transfer coefficient of Na ($\tau_{Na}$) in the profile presents a negative value, indicating a loss during chemical weathering. The changes of $\tau_k$ are similar to those of $\tau_{Na}$ in the whole section. K mainly occurs in minerals such as potassium feldspar, biotite, and hornblende, and mineral weathering leads to the loss of K [140]. But $\tau_k$ is abnormally enriched in the semi-weathered layer and saprolite layer, suggesting the possibility of external dust (such as potassium feldspar) input [110]. Compared with $\tau_k$ and $\tau_{Na}$, the $\tau_{Ca}$ and $\tau_{Mg}$ present positive values in the profile, indicating the enrichment of Ca and Mg in the profile. It is generally believed that Ca occurs mainly in feldspar minerals, while Mg occurs mainly in biotite and hornblende. With the process of weathering, Ca and Mg elements leach from primary minerals, but minerals such as mica and feldspar transform into secondary clay minerals in the profile, and Ca and Mg can be adsorbed in clay minerals and re-precipitated [141,142]. Therefore, Ca and Mg are abnormally enriched in the weathering profile.

![Figure 10. Mass transfer coefficients of the mobile elements Na, K, Ca, and Mg, and the immobile elements Si, Al, and Fe in the granite weathering profile.](image)

In addition to the mobile elements, we also evaluated the mass transfer coefficients of three relatively immobile elements in the profile (Figure 10). The Si activity is poor in the weak weathering process, but $\tau_{Si}$ shows positive values in the semi-weathered layer and saprolite layer, indicating the enrichment of Si, which is related to the dust input of Si-containing minerals (such as quartz) [143]. Fe is significantly enriched in the profile ($\tau_{Fe} > 0$), and because Fe is a variable valence element, it can be enriched in the profile in the form of oxides due to oxidation reactions during weathering. Al mostly exists in the form of stable oxides and hydroxides or occurs in clay minerals in weathering profiles, but $\tau_{Al}$ presents a negative value in some layers of the profile, which may be caused by the acidic environment of the profile [144].

Heavy minerals, with a strong resistance to weathering and abrasion in rocks, have the characteristics of stable properties and a good inheritance from parent rocks [145–148]. In this study, the heavy mineral assemblages of the weathering samples are similar to those of the parent rocks, mainly consisting of zircon, ilmenite, and hematite-limonite. With the weathering of the granite, the hematite-limonite contents show an increasing trend. We speculate that the increase of hematite-limonite contents during weathering is caused by the conversion of ferromagnetic minerals such as magnetite into hematite-
Limonite [149]. In order to demonstrate this view, we analyzed the magnetic susceptibility of the weathered products in the profile, and the results show that the magnetic susceptibility values gradually decrease from the bottom to the top, which indicates a decline in the magnetic minerals. In addition, during the artificial identification of heavy minerals, it was found that magnetite is black-brown, red-brown, and mostly in hematitizations, which also proves the weathering origin of some hematite-limonite from magnetite.

Above all, in the process of rock weathering, weathering products have good parent rock inheritance. With the progress of weathering, unstable minerals such as feldspar and mica decompose, leading to the leaching of mobile elements such as Na and K, and the adsorption of secondary minerals makes Ca and Mg elements accumulate in the profile. Stable heavy minerals such as hematite-limonite, zircon, and ilmenite have little change in the profile. The transformation of magnetite into hematite-limonite during chemical weathering results in an increase in hematite-limonite in the profile and the disappearance and decomposition of magnetite.

4.3. Influence of Foreign Substances

During rock weathering, the mobile element Sr can be released inconsistently from weathering minerals (such as feldspar), and \(^{87}\text{Sr}/^{86}\text{Sr}\) shows a decreasing trend with the weathering process [150–155]. In the process of granite weathering, the Sr isotopic changes include four stages: (I) a decreasing trend of \(^{87}\text{Sr}/^{86}\text{Sr}\), related to the weathering decomposition of biotite [155]; (II) the rapid increase of \(^{87}\text{Sr}/^{86}\text{Sr}\), due to the decomposition of plagioclase with weathering and the leaching of Sr with lower \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios; (III) the gradual decrease of \(^{87}\text{Sr}/^{86}\text{Sr}\): in this third stage, the weathering rate of potassium-containing minerals (such as potassium feldspar, illite, and residual biotite) increases relatively, and \(^{87}\text{Sr}/^{86}\text{Sr}\) becomes higher with the release of K, Rb, and radioactive Sr; and (IV) a gradually stable \(^{87}\text{Sr}/^{86}\text{Sr}\) value: at this time, the rock is completely weathered and the Sr in the rock is all leached, so the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio does not change [156].

In this study, the Sr isotopic ratios in the granite weathering profile show complex variations, with values clearly lower than those in the granite parent rock. In the semi-weathered layer, the \(^{87}\text{Sr}/^{86}\text{Sr}\) values decrease rapidly, which may be related to the addition of foreign substances with low \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios. The study area is located downwind of the Songnen Sandy Land, so we believe that the addition of dust materials of low \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios from the Songnen Sandy Land has resulted in the decrease in the \(^{87}\text{Sr}/^{86}\text{Sr}\) values in the weathering profile [157]. In the saprolite layer, the \(^{87}\text{Sr}/^{86}\text{Sr}\) values increase slowly. The addition of foreign substances weakens the influence brought by the decomposition of plagioclase, leading to a trend of slow increase in this stage. In the oxidized soil layer, the \(^{87}\text{Sr}/^{86}\text{Sr}\) values slowly decrease, which is consistent with the standard weathering trend and is affected by the increase in the weathering rate of potassium-containing minerals. However, the Sr isotopic composition of the weathering granite in this study does not go through the fourth stage, which is mainly restricted by the chemical weathering degree. The chemical weathering degree in this profile is low, and the Sr-containing minerals cannot be completely decomposed under the low degree of chemical weathering, so the \(^{87}\text{Sr}/^{86}\text{Sr}\) values cannot reach a stable state. Accordingly, the addition of foreign substances in the formation process of the weathering profile leads to abnormal changes in \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio.

The Nd isotopic composition of sediments is only affected by the parent rock lithology and is basically not affected by chemical weathering [158]. It is accepted that the difference of between-sample Nd isotopic ratios (\(\varepsilon\text{Nd}(0)\)) can be considered to be controlled by geological factors rather than experimental error only if the difference is greater than 1 \(\varepsilon\) unit [157]. In this study, the variation ranges of the \(\varepsilon\text{Nd}(0)\) values in the semi-weathered layer and the saprolite layer are significantly greater than 1, indicating the changing Nd isotopic composition [159]. Notably, the \(\varepsilon\text{Nd}(0)\) values in the weathering products are markedly lower than those in the granite parent rock. These observations collectively indicate the addition of external heterologous materials to these weathering layers.
Independent tracer elements Th and Zr can reflect the correlation between the rock weathering products and the parent rock and can be used to test whether there is the addition of foreign substances in the weathering process of granite. This study showed that the weathering samples from granite parent rocks evolve along a single Th/Zr trend line, while the weathering samples with foreign material input evolve along a different trend line [160]. In this study, the Th/Zr trend line correlation between the weathering samples and the parent rock is weak ($R^2 = 0.2276$) (Supplementary Figure S4), which indicates the existence of foreign material input during granite weathering.

In addition, we selected the CDF value, a stable index that can represent the quality change of profile elements, to calculate the weathering products. The CDF can reflect the mass loss of profile elements, where a CDF < 0 represents the input of foreign substances [110]. The calculated results show that the CDF values of the semi-weathered layer and the saprolite layer are less than 0, which further proves the input of foreign substances in the process of granite weathering.

4.4. Effects of Biological Activities

In addition to the addition of foreign materials, biological activities may also have an effect on granite weathering. Studies have shown that in the natural environment, organisms control the dissolution of minerals and migration of elements mainly through the dissolution and complexation of organic acids [161–164] to obtain the necessary nutrients for life activities, which is the main control factor of biological weathering [165,166]. Organic acids are usually secreted by Proteusbacillus vulgaris, actinomycetes, and Acidobacteria [167] and are complex with cations on mineral surfaces or in solution [168], allowing the element to migrate within the profile. The study on the complexation ability of organic acids and cations showed that they have a strong complexation ability to the Al element, which can avoid the adsorption and precipitation of Al in clay minerals [169]. The abiotic element migration experiment showed that in weathering systems without organic acid secretion, the amount of Al lost during weathering is lower [168,170], but in weathering systems with the presence of organic acids, the loss rate of Al during weathering increases by 2–3 orders of magnitude [170]. Therefore, the migration and enrichment degree of the Al element can be used as a key index to measure the influence of biological action on rock weathering.

In order to quantify Al mobility in the weathering profiles, we normalized the Al elements. The Ti element has poor binding ability with organic acids, is only affected by chemical weathering in a natural weathering environment, and is not easy to migrate in the profile, so it could exist as a fixed element in the profile [170]. Therefore, Ti is selected as a fixed element to normalize Al and the calculation formula is as follows:

$$\Delta Al/Ti = \frac{(Al/Ti)_{\text{weathered}}}{(Al/Ti)_{\text{parent}}} - 1$$

where, $(Al/Ti)_{\text{weathered}}$ represents the Al/Ti ratio in weathering products, and $(Al/Ti)_{\text{parent}}$ represents the Al/Ti ratio in the parent rock. $\Delta Al/Ti < 0$ indicates Al loss relative to Ti during weathering, which means that the profile is affected by biological weathering. A $\Delta Al/Ti > 0$ indicates that Al is enriched relative to Ti during weathering and can also reflect the effect of organic acids secreted by organisms on profiles. The profile with an average $\Delta Al/Ti \approx 0$ indicates no evidence of organic acid weathering [160].

The $\Delta Al/Ti$ values in the weathering products in this study show positive values at the bottom of the weathering profile and negative values at the rest, indicating biological activities during the formation of the weathering profile. In the weathering profiles, the organic acids secreted by organisms cause the Al element to be unable to be fixed in clay minerals or reprecipitate during weathering, so Al is deficient relative to the Ti element. At the bottom of the profile, the positive $\Delta Al/Ti$ values are likely to be caused by the decomposition of the Al element at the top of the profile through the organometallic complex transported surface or groundwater and its pooling at the bottom [160]. In addition, the
average $\Delta$Al/Ti value of $-0.29$ in the granite weathering profiles indicates the influence of a certain degree of biological activities on the weathering products.

The frequency-dependent susceptibility is determined by the content of the superparamagnetic minerals formed by pedogenesis, and high frequency-dependent susceptibility in the profile indicates the presence of superparamagnetic minerals in the sample, which is closely related to biological factors. A large number of superparamagnetic magnetite particles can be synthesized by a bioinduced (extracellular) and biocontrolled (intracellular) reduction in Fe$^{3+}$ [171,172]. The $\chi_{fd}\%$ value (5%–6%) for superparamagnetic particles exists in critical standards [173,174]. The average $\chi_{fd}\%$ of the weathered samples is 14.79%, indicating the formation of more superparamagnetic particles in the weathering process under the influence of biological action. Two high $\chi_{fd}\%$ values, at the top of the oxidized soil layer and the top of the saprolite layer, indicate the increasing contents of superparamagnetic particles formed by pedogenesis with a bioperturbation effect. However, the low $\chi_{fd}\%$ values in the semi-regolith layer indicate fewer effects from biological action.

Finally, the geochemical genes constructed in this study also give additional information about the addition of biological activities to the development of the weathered profile. The similarity between the LG01 genes of the weathering products and the parent rock significantly fluctuates, whereas the LG03 genes, which remove the influence of foreign materials and biological activities, are clearly stable and have a high similarity with the parent rock (R > 95%), to a certain extent also indicating the effect of biological activities.

4.5. Environmental Significance of the Granite Weathering Profile

Rock weathering is mainly controlled by two end-members, supply-limited and kinetic-limited weathering [1,24,39–41,175,176]. A kinetic-limited weathering regime usually occurs in environments with high erosion rates or weak hydrological cycles, where fresh, easily weathered rock-mineral particles are more affected by water-rock processes, and the degree of rock weathering is limited by climatic environments such as temperature and precipitation. During weathering, active metal cations (such as Na$^+$, Ca$^{2+}$, and K$^+$) are continuously leached from the primary minerals, but the degree of leaching is low, so the chemical weathering process is limited to the initial stage [1,45,46,177]. For a supply-limited weathering regime, the warm and humid climate environment provides sufficient water and acid for rock weathering, the rock can fully react with water and acid, and the active metal cations in the fresh regolith can also be completely leached. In this case, most of the silicate minerals are decomposed, and the weathering rate of the rock is limited by the physical erosion rate. Therefore, the degree of rock weathering depends on the supply rate of fresh minerals. Physical denudation increases in tectonically active areas which can provide fresh minerals for rock weathering and aggravate the degree of rock weathering [42–44]. In conclusion, the supply-limited weathering regime mostly belongs to tectonically stable situations with high temperatures and precipitation, and consequently high chemical weathering but low physical erosion rates. However, the kinetic-limited weathering regime is characterized by limited temperature and precipitation (e.g., low temperature and precipitation), mostly belonging to tectonic uplift scenarios with high erosion rates but low chemical weathering degree.

Guo et al. (2022) pointed out that areas with CIA > 80 are dominated by supply-limited weathering regimes, while areas with CIA < 80 are dominated by kinetic-limited weathering regimes. The critical MAP (Mean Annual Precipitation) for CIA = 80 is 1000 mm and the critical MAT (Mean Annual Temperature) is 15 $^\circ$C. But this threshold is not immutable, and once the balance between kinetically-limited and supply-limited regimes is broken, the two can be transformed into each other [178]. Therefore, we can reasonably speculate that the increasing annual mean precipitation and ongoing global warming may result in an expansion in the supply-limited weathering areas, while conversely, cooling may lead to the expansion of the kinetic-limited weathering areas. During the Paleocene–Eocene Thermal Maximum (PETM), the global temperature increased and the silicate weathering regimes changed into supply-limited weathering regimes, which is related to the increase
in the silicate weathering rate caused by the rising temperature [179,180]. During the Eocene/Oligocene (E/O) transition, the global silicate weathering regimes transformed into kinetic-limited weathering regimes due to greater CO$_2$ absorption and accelerated global cooling [181]. In addition, a tectonic uplift [182] and/or an intensified hydrological cycle [183,184] can produce more weatherable materials, resulting in a shift from the supply-limited weathering regimes to the kinetic-limited weathering regimes, increasing silicate weathering rates and CO$_2$ consumption, and accelerating global climate cooling [181–183]. The CIA can be used to evaluate the change in silicate weathering regimes in a weathering environment [40,185]. The CIA values of the studied weathering profile are much less than 80. In order to further study the types of regional weathering regimes, the CIA values of some sedimentary sections in the region that do not undergo post-sedimentary diagenesis and weathering recycling were collected (Supplementary Table S3) to show that the average CIA values of all sections are much less than 80, indicating a low weathering degree in the region [186–188]. Therefore, according to the regional CIA value, we believe that the weathering pattern in the Harbin area is marked by the kinetic-limited weathering regime with a mechanical erosion rate higher than the chemical weathering rate, which inhibits the leaching of mobile cations from the weathering profile. A strong weathering profile is difficult to form under such strong denudation, resulting in weak weathering in the region [189]. However, this conclusion seems to contradict the understanding that a kinetic-limited weathering regime mostly occurs in tectonically active areas, because there was no obvious evidence of tectonic uplift during the development of the weathering profiles [97,190].

According to the classical weathering theory, in the vertical weathering profile [110,111,125], the weathering degree progressively increases with decreasing depth [191]. However, the chemical weathering degree in the studied profile exhibits the opposite pattern (Figure 7), unique to this region. The low level and unique shifting pattern of the weathering degree in the profile, combined with calm tectonic characteristics during the development of the weathering profile, together indicate that the regional weathering regimes have not changed during the process of the granite weathering in the studied region and the kinetic-limited weathering regimes are dominant. More precisely, the weathering characteristics in the profile reveal this region to be a kinetic-limited weathering regime with a supply-limited weathering nature.

5. Conclusions

The heavy minerals, geochemistry, magnetic susceptibility, and chromaticity investigation of the Yingjie granite weathering profile reveals the following conclusions:

1. The granite has experienced a combination of physical and chemical weathering during the weathering process. The physical weathering is strong, resulting in a large number of cracks in the rock, while the chemical weathering process occurs mainly in the initial stage, as the highly-developed chemical weathering profile cannot develop because of the intervention of physical weathering before chemical weathering produces highly weathered minerals.

2. The binary diagram (e.g., TiO$_2$-Zr, and La/Sc-Co/Th) and geochemical genes (LG01 and LG03) reveal that the weathering products have a good inheritance from the parent rock. The influence of chemical weathering on the granite parent rock can be revealed through the characteristics of the elements and minerals in the weathering products.

3. The Sr-Nd isotope, Th/Zr ratio, and CDF indicate an input of external materials during granite weathering. The DAl/Ti ratios and χfd% indicate the existence of biological activities during granite weathering. At the same time, the geochemical gene (LG03) also indicates the influence of the addition of external materials and biological activities on the weathering of granite.

4. A comprehensive analysis shows that the Yingjie granite weathering profile belongs to the kinetic-limited weathering profile with a limited supply, and the weathering regime of the profile does not vary in geology time. The low temperature, low precipitation, and weak hydrological cycle in the study area inhibit the leaching of
mobile cations from the regolith, resulting in rock weathering at the initial stage of chemical weathering.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/min14010017/s1, Text S1: Methods of constructing geochemical genes; Figure S1: ANK-ACNK diagram and SiO2-K2O diagram of the Granite bedrock; Figure S2: Chondrite-normalized rare-earth element patterns in the profile; Figure S3: The relationship between immobile elements Zr, Ti, and Nb in the weathering profile; Figure S4: Th/Zr trend lines for the weathered and host rock samples; Table S1: Sr-Nd isotopic composition in the studied weathering profile; Table S2: Granite weathering profile LG01, LG03 gene coding and similarity R%; Table S3: Weathering degree of regional sedimentary profile. Refs. [82–84,118,132,186–188,192,193] were cited in the Supplementary Materials.

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