

Article

C, N, and P Stoichiometry Characteristics of Fresh and Weathered Sandstones in Longhushan Area, SE China

Yunni Chang^{1,2}, Chaobin Xu^{1,2,*}, Junting Qiu³, Josep Peñuelas^{4,5}, Jordi Sardans^{4,5}, Hanzhao Zeng², Quanlin Zhong^{1,2} and Baoyin Li^{1,2,*}

¹ Fujian Provincial Key Laboratory for Plant Eco-Physiology, Fujian Normal University, Fuzhou 350007, China

² College of Geographical Sciences, Fujian Normal University, Fuzhou 350007, China

³ National Key Laboratory of Science and Technology on Remote Sensing Information and Image Analysis, Beijing Research Institute of Uranium Geology, Beijing 100029, China

⁴ CREAM, Cerdanyola del Vallès, 08193 Barcelona, Spain

⁵ Global Ecology Unit CREAM-CSIC-UAB, CSIC, Bellaterra, 08193 Barcelona, Spain

* Correspondence: author: xuchaobin@fjnu.edu.cn (C.X.); liby@fjnu.edu.cn (B.L.)

Abstract: Carbon (C), nitrogen (N), and phosphorus (P) stoichiometry and their allometric relationships in soil and plants are hot topics that attract a lot of attention, while those rocks that form soils are often neglected. Weathering is a common geological phenomenon that may significantly influence the nutrient composition and release of nutrients from rock and its inherent soils. This study presents C, N, and P concentrations data as well as microscope petrological photographs of fresh and weathered sandstones from Longhushan World Geopark in SE China, in an attempt to investigate C, N, and P stoichiometry of rocks before and after weathering and discuss the driving mechanisms. The results show that weathering significantly decreased rock C, C/N, and C/P concentrations, slightly decreased N and N/P concentrations, and slightly increased P concentration. Microscope observations show that fresh sandstones contain calcite, apatite, microplagioclase, and organic matter, while weathered sandstones feature apatite and organic matter. The flexible allometric relationships and mineral changes before and after rock weathering indicate that chemical mechanisms, such as dissolution of carbonate and hydration of microplagioclase, have changed the existence form of C, N, P and, thus, significantly influence rock C, N, and P stoichiometry. This stoichiometry feature can be in turn used to reflect the regulation effect of rock weathering.

Keywords: weathering; C N and P stoichiometry; allometric relationship; Danxia landform rocks



Citation: Chang, Y.; Xu, C.; Qiu, J.; Peñuelas, J.; Sardans, J.; Zeng, H.; Zhong, Q.; Li, B. C, N, and P Stoichiometry Characteristics of Fresh and Weathered Sandstones in Longhushan Area, SE China. *Minerals* **2023**, *13*, 483. <https://doi.org/10.3390/min13040483>

Academic Editor: Daniel Tunega

Received: 25 December 2022

Revised: 19 March 2023

Accepted: 23 March 2023

Published: 29 March 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

Carbon (C), Nitrogen (N), and Phosphorus (P) stoichiometry and their allometric relationship are important indicators of energy flow, nutrient circulation, and terrestrial biogeochemical processes [1–3]. Carbon is the basis of plant growth, reproduction, and structure, and structural material of living organisms [4]. Nitrogen is a limiting element in all kinds of ecosystems on the earth's surface and an essential nutrient element for plant growth and one of the main factors for the productivity of terrestrial ecosystems [5]. Phosphorus is an essential element for terrestrial ecosystems and, also, a key limiting nutrient element for terrestrial primary productivity, which is widely involved in important metabolic processes of living organisms [6,7]. Due to the coupling of chemical functions and the irreplaceability of these elements, the demand and utilization of C, N, and P in terrestrial ecosystems follow a certain proportion among them [8–10]. C, N, and P stoichiometry is a powerful and effective tool to predict the scaling of biomass production, trophic dynamics, and nutrient limitation in terrestrial ecosystems [9,11,12]. It was reported that stoichiometry is considered an important index for substrate use efficiency [13]. The scaling relationship has widely been used to analyze the C, N, and P partitioning in an organism (i.e., cellular, biological, ecosystem) based on its invariance rules and allometric relationships [14,15] and

based on their asymmetrical participation in the structures and functions of the distinct organism [16]. The scaling relationship can be described by the equation $y = \beta x^\alpha$, where y and x are nutrient concentrations, α and β represent the scaling exponent (slope) and the normalization constant (intercept), respectively. When α equals 1, the relationship represents an isometric scaling relationship; $\alpha \neq 1$ indicates an allometric relationship. There is no consensus on the scaling relationship of C, N, and P relationships. For example, the 2/3 and 3/4 power laws of leaf N vs. leaf P were obtained from pooled data [17,18]. The scaling relationships are sensitive to climate, soil, and a variety of other abiotic factors, which may be an important mediator of the most significant ecosystem processes.

Sedimentary rock occupies about 65% of the terrestrial land surface [19]. It is one of the main material sources for soil and, thus, can influence soil element composition, properties, and quality [20]. It is also an important source of nutrients that benefit plant growth and the terrestrial ecosystem directly or indirectly [20–22]. Previous reports showed that forests associated with soils generated from N-rich rocks contain 42% more carbon in aboveground tree biomass and 60% more carbon in the upper 30 cm of the soil than those associated with soils generated from N-poor rocks [23]. Additionally, the nutrients derived from rocks play an important role in the regional and global geochemical cycle [23,24].

Recently, scientists began to focus on the elemental stoichiometric characteristics of rock [24]. Some studies demonstrate that emitted rock N due to the rock weathering process may be an important and overlooked component of ecosystem N and C cycling, and 19 to 31 teragrams of nitrogen are mobilized from near-surface rock annually in the earth's surface environment [23,24]. In addition, soil P has also been demonstrated to be mostly derived from weathered rock. Although the significance of element input from rock due to rock weathering has been demonstrated and agreed upon in previous studies, the C, N, and P stoichiometry characteristics and the scaling relationship of weathered and unweathered rocks, as well as the driving mechanism during weathering process remain obscure.

In this study, we collected the sandstone samples from the Danxia landform in Longhushan Mountain World Geopark of Jiangxi Province and investigated and compared the element concentrations of fresh and weathered sandstones, in an attempt to discuss: (1) the stoichiometry characteristics and allometric relationships of sandstones C, N, and P associated with the Danxia landforms; (2) the impact of weathering on the characteristics and allometric relationship of stoichiometric of Danxia sandstones; and (3) the driving mechanism of stoichiometric change of sandstone during the weathering process. The results contribute to a better understanding of the regional as well as global C, N, and P cycle.

2. Study Area

The study area is located in Longhushan of Guixi City, southwest of Yingtan City, Jiangxi Province in southeast China (Figure 1), which is a transitional zone between Wuyi Mountains and Poyang Lake Plain. The climate in this region is classified as a subtropical humid monsoon climate. The average annual temperature is 17.9 °C, the average precipitation is 1750 mm. The soil is classified as red soil in the Chinese soil classification system. The vegetation of the cliff tops is xerophytic, including *Pinus massoniana*, *Castanopsis sclerophylla*, *Cyclobalanopsis glauca*, *Juniperus formosana*, and *Moringa oleifera* [25]. The landform is mountainous and hilly. It includes almost all kinds of the Danxia landforms in a subtropical humid area, in which the single form includes a cliff, stone wall, peak, valley, and others, and the group form is characterized by the eroded residual broad valley peak cluster, peak forest, isolated peak, and residual hill [26].

Tectonically, the Longhushan area is located in the confluence zone of the Yangtze plate and Cathaysian plate and the southern margin of the middle section of the Mesozoic Xinjiang fault basin. The regional strata include a relatively complete quaternary sequence from Lower Proterozoic to Cenozoic. The strata exposed in the Longhushan area are mainly the Hekou formation and the Tangbian formation of the Late Cretaceous. The Hekou formation is characterized by purplish-red medium-thick layered conglomerate sandstone;

Tangbian formation is characterized by purplish-red, brick-red rock intercalated with grayish-green sandstone, siltstone, and mudstone and locally intercalated with (containing) gravelly sandstone and gypsum [26,27].



Figure 1. The geographic map shows the location of the Longhushan area.

3. Materials and Methods

3.1. Sampling

The sampling sites were located in the hilly ground outside the Danxia landform in Longhushan World Geopark, Jiangxi Province. Seven different sites were selected for sample collection in March 2017. Fresh purplish-red sandstone, as well as weathered and discolored or white sandstone in purplish-red sandstone, was collected with a hammer (Figure 2). Fresh sandstone samples were collected from the bedrock that was not exposed to the surface while weathered sandstone samples had been exposed to the surface for a long time as some parts of the sample had obvious fading [28]. A total of 42 samples were cut or knocked away from surface contaminants, such as mud coats, dust covers, and other potential deposited materials, and cleaned carefully. Each cleaned sample was divided into two parts. The first part was used for rock total C, N, and P concentration analyses, and the second part was used for petrological and mineralogical analysis.



Figure 2. Typical photos show fresh (purplish-red) and weathered (discolored or white) sandstones.

3.2. Rock Total C, N, and P Concentration Determination

The first part of sample was reduced to rock pieces of 1–2 cm in size using a percussion mill and powdered with a thoroughly cleaned agate mill, then analyzed with a carbon-

nitrogen analyzer (Elementar Vario EL III; Elementar, Langenselb, Germany) and the molybdenum-antimony anti-colorimetric method [29] to determine rock total C, N, and P concentrations, respectively.

3.3. Petrological Mineralogical Analysis

The second part of the sample was cut using a slab saw, then reduced in size to slightly smaller than a thin section using a trim saw. The cut and reduced rock chips were polished to remove marks from the saw blade on their surfaces, then glued to glass slides with epoxy. The rock chips epoxied to glass slides were cut off and ground to 30 μm thick, then covered with thin glass slips to protect them from damage. The rock sections were photographed using a PDV-SW-200S microscope equipped with a polarizer. The micrographs of the sections were taken by a digital photographic system of PDV-HDMI-1400V.

3.4. Data Analyses

All data analyses were conducted in SPSS 26.0 software and R version 3.6.1. The data were log-transformed to meet normality, and the effects of rock weathering on rock C, N, and P concentrations were analyzed by the *t*-test using SPSS 26.0. We also selected Hedge's *d* to calculate the effect size for rock C, N, and P stoichiometry among different rock types. The effect size of Hedge's *d* was calculated according to the equation [30,31]: $d = [(X^E - X^C)/S] \times J$, where X^E is the mean of weathered rock, X^C is the mean of fresh rock, *S* is the pooled standard deviation, and *J* is a weighting factor that is calculated according to Yang [31]. $J = 1-3 / [4(N^C + N^E - 2) - 1]$, *N* was the sample size. The effect size was calculated using the "esc" package in R v. 3.6.1. The standardized major axis (SMA) regression was used to describe the scaling relationship among the elements. A common scaling slope was quantified with no statistically significant differences in the numerical values of α among fresh and weathered rock. The significance level for testing slope heterogeneity was set at $p < 0.05$. The SMA was performed using the "smart" package in R v. 3.6.1.

4. Results

4.1. Rock Total C, N, and P Concentrations

The C, N, and P concentrations of the collected rock samples are in the range of 41 mg g^{-1} to 680 mg g^{-1} , 3.1 mg g^{-1} to 20 mg g^{-1} and 2.4 mg g^{-1} to 6.5 mg g^{-1} , respectively. The C/N, C/P, and N/P ratios are ranging from 6.03 to 210, 6.5 to 290, and 0.51 to 7.6, respectively. It is clear that rock C, C/N, and C/P concentrations were significantly decreased, N and N/P concentrations were slightly decreased, and P concentration was slightly increased after the weathering process (Figures 3 and 4).

4.2. Allometric Relationship of C, N, and P Stoichiometry between Fresh and Weathered Rocks from Longhushan Area

There was no significant correlation among rock C, N, and P concentrations before and after weathering (Table 1). According to the SMA regression, the scaling slopes of C and N and N and P in the fresh and weathered sandstone did not differ significantly, with a common slope of -0.66 ($-0.93 \sim -0.49$, $p = 0.45$) and -1.61 ($-2.36 \sim -1.20$, $p = 0.06$), respectively. The scaling slopes of C and P differed significantly and decreased from the fresh sandstone (-1.29) to the weathered sandstone (-0.31). C concentration exhibited strong positive correlations with C/N and C/P in the fresh sandstone ($p < 0.001$). N concentration was significantly positively correlated with N/P in the fresh sandstone ($p < 0.001$). N concentration was significantly negatively correlated with C/N in the two rock types ($p < 0.001$; $p = 0.003$), with a common slope of -0.71 . P concentration exhibited strong negative correlations with C/P and N/P in the two rock types ($p < 0.001$; $p = 0.003$). C/N was significantly positively correlated with C/P and negatively correlated with N/P ($p = 0.002$; $p < 0.001$), with an SMA regression slope of 1.25 and -1.05 , respectively.

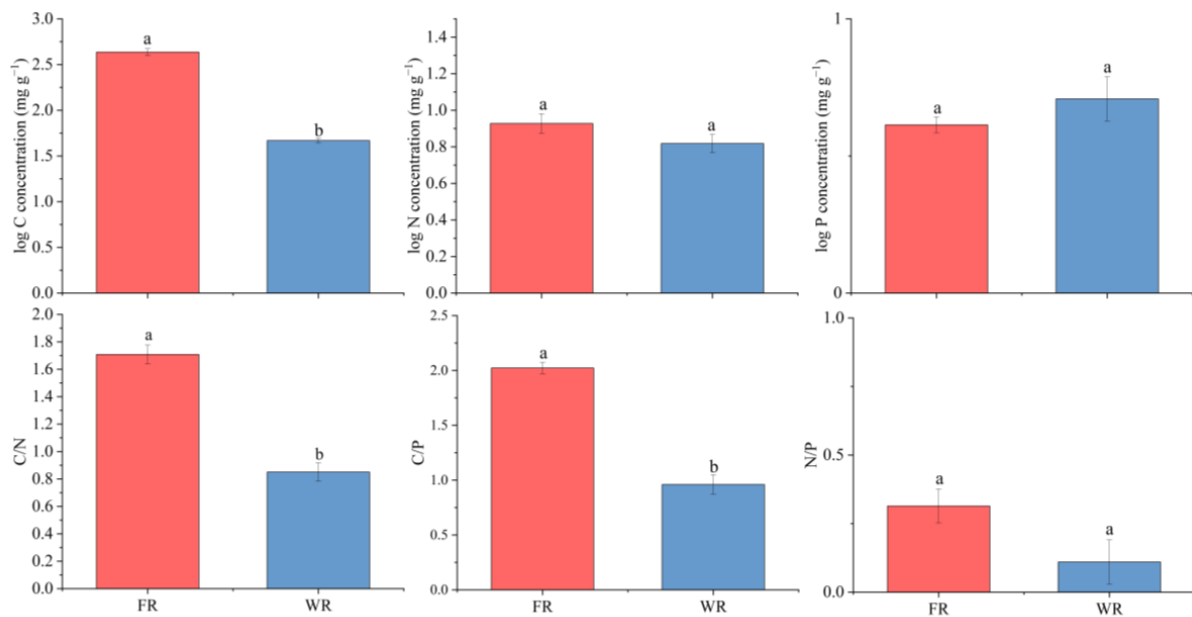


Figure 3. Rock C, N, and P stoichiometry in two rock types. Note: FR: fresh rock. WR: weathered rock. C and P data are reported in this study. N data are sourced from [26]. Error bars indicate SE. Different letters of a and b indicate that values are significantly different at the $p = 0.05$ level between the two rock types.

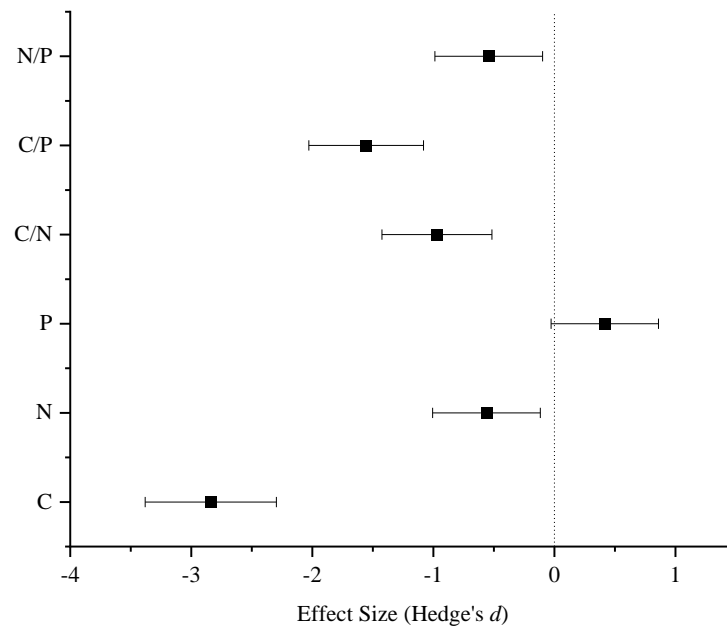


Figure 4. The effect size of rock C, N, and P concentrations, and stoichiometry response to weathering (Error bars represent $\pm 95\%$ CI).

Table 1. Standardized major axis (SMA) regression analysis on the scaling relationships between the C, N, and P stoichiometry of fresh and weathered rock of the Danxia landform.

Index ($y - x$)	Type	Slope (95%CI)	Intercept (95%CI)	R^2	p	Common Slope	p	Intercept
C-N concentrations	fresh	-0.70 (-0.98, -0.50)	3.29 (3.04, 3.53)	0.01	0.50	-0.66 (-0.93, -0.49)	0.45	3.2 a
	weathered	-0.49 (-1.31, -0.18)	2.07 (1.60, 2.54)	0.31	0.25			2.2 b

Table 1. Cont.

Index ($y - x$)	Type	Slope (95%CI)	Intercept (95%CI)	R ²	<i>p</i>	Common Slope	<i>p</i>	Intercept
C-P concentrations	fresh	−1.29 (−1.80, −0.92)	3.43 (3.14, 3.71)	0.04	0.24		0.02	
	weathered	−0.31 (−0.94, −0.10)	1.88 (1.57, 2.20)	0.02	0.77			
C concentration- C/N	fresh	0.55 (0.42, 0.71)	1.70 (1.45, 1.96)	0.40	<0.001	0.51 (0.40, 0.67)	0.28	1.8 a
	weathered	0.37 (0.17, 0.80)	1.36 (1.08, 1.63)	0.62	0.065			1.2 b
C concentration- C/P	fresh	0.72 (0.60, 0.87)	1.18 (0.89, 1.46)	0.70	<0.001	0.69 (0.58, 0.85)	0.078	1.2 a
	weathered	0.28 (0.10, 0.80)	1.40 (1.05, 1.75)	0.18	0.40			1.0 b
C concentration- N/P	fresh	−0.60 (−0.85, −0.43)	2.83 (2.70, 2.95)	0.01	0.98	−0.54 (−0.78, −0.40)	0.088	2.8 a
	weathered	−0.22 (−0.69, −0.07)	1.69 (1.59, 1.80)	0.02	0.79			1.7 b
N-P concentrations	fresh	−1.84 (−2.58, −1.30)	2.05 (1.63, 2.47)	0.01	0.81	−1.61 (−2.36, −1.19)	0.055	1.9 a
	weathered	−0.62 (−1.81, −0.21)	1.26 (0.67, 1.85)	0.15	0.45			1.9 a
N concentration- C/N	fresh	−0.78 (−0.94, −0.64)	2.26 (2.00, 2.51)	0.71	<0.001	−0.77 (−0.91, −0.65)	0.83	2.2 a
	weathered	−0.75 (−1.13, −0.50)	1.45 (1.18, 1.73)	0.91	0.003			1.5 b
N concentration- C/P	fresh	−1.03 (−1.45, −0.73)	3.01 (2.27, 3.75)	0.01	0.73	−0.95 (−1.36, −0.70)	0.29	2.8 a
	weathered	0.57 (0.19, 1.74)	0.27 (−0.50, 1.04)	0.04	0.71			1.7 b
N concentration- N/P	fresh	0.86 (0.73, 1.02)	0.66 (0.59, 0.73)	0.78	<0.001	0.84 (0.72, 0.99)	0.12	0.67 a
	weathered	0.46 (0.20, 1.05)	0.77 (0.65, 0.89)	0.55	0.094			0.73 a
P concentration- C/N	fresh	−0.42 (−0.60, −0.30)	1.34 (1.07, 1.60)	0.01	0.65	−0.48 (−0.64, −0.33)	0.072	1.4 a
	weathered	1.20 (0.40, 3.64)	−0.31 (−1.73, 1.10)	0.05	0.66			1.1 b
P concentration- C/P	fresh	−0.56 (−0.72, −0.44)	1.75 (1.46, 2.03)	0.50	<0.001		0.027	
	weathered	−0.92 (−1.34, −0.63)	1.59 (1.24, 1.93)	0.92	0.002			
P concentration- N/P	fresh	−0.47 (−0.63, −0.35)	0.76 (0.69, 0.83)	0.26	0.002	−0.54 (−0.69, −0.39)	0.12	0.79 a
	weathered	−0.73 (−1.27, −0.42)	0.79 (0.67, 0.91)	0.82	0.012			0.77 a
C/N-C/P	fresh	1.32 (0.98, 1.78)	−0.97 (−1.79, −0.15)	0.25	0.002	1.25 (0.95, 1.70)	0.33	−0.82 a
	weathered	0.76 (0.25, 2.37)	0.12 (−0.94, 1.18)	0.01	0.99			−0.35 a
C/N-N/P	fresh	−1.11 (−1.42, −0.86)	2.06 (1.91, 2.20)	0.47	<0.001	−1.05 (−1.36, −0.83)	0.20	2.0 a
	weathered	−0.61 (−1.58, −0.23)	0.91 (0.72, 1.11)	0.36	0.21			0.97 b
C/P-N/P	fresh	0.84 (0.60, 1.16)	1.76 (1.60, 1.91)	0.08	0.097	0.83 (0.62, 1.11)	0.89	1.8 a
	weathered	0.80 (0.37, 1.72)	0.87 (0.68, 1.06)	0.63	0.060			0.87 b

Different lowercase letters indicate significance between the fresh and weathered bedrock at $p < 0.05$ level.

4.3. Petrology, Mineral Composition

Both fresh and weathered sandstone samples are poorly to moderately sorted (Figure 5a). The framework grains are mainly composed of quartz (80% to 90%) and feldspar (10% to 15%) (Figure 5b,c). Quartz grains are low spherical or angular to subangular in shape with grain size generally ranging from $20 \times 50 \mu\text{m}$ to $100 \times 250 \mu\text{m}$ (Figure 5a). Feldspar includes plagioclase and microcline. Plagioclase grains are subangular to rounded in shape and usually $20 \times 50 \mu\text{m}$ to $100 \times 150 \mu\text{m}$ in size with clear polysynthetic twinning (Figure 5b). Microcline grains are subangular to rounded in shape and generally $50 \times 100 \mu\text{m}$ to $100 \times 150 \mu\text{m}$ in size. The microcline grains can be divided into two groups: the first group is characterized by tartan twinning, which can be found in fresh samples (Figure 5c), while the second is dirty on their surface due to kaolinite alteration (Figure 5d), which can be observed in some weathered samples. Calcite cementations that are characterized by rhombic cleavage (Figure 5e) can be found in pore spaces or gaps between mineral grains in fresh samples (Figure 5f) and can be hardly found in weathered samples. Apatite can be observed in both fresh and weathered samples as columnar inclusions in mineral fissures (Figure 5g) or individual grains (Figure 5h). Additionally, organic matter can be found in fresh and weathered samples and hematite can be found in fresh samples. Through reflected light, hematite is brownish-red in color while the organic matter is black in color (Figure 5i).

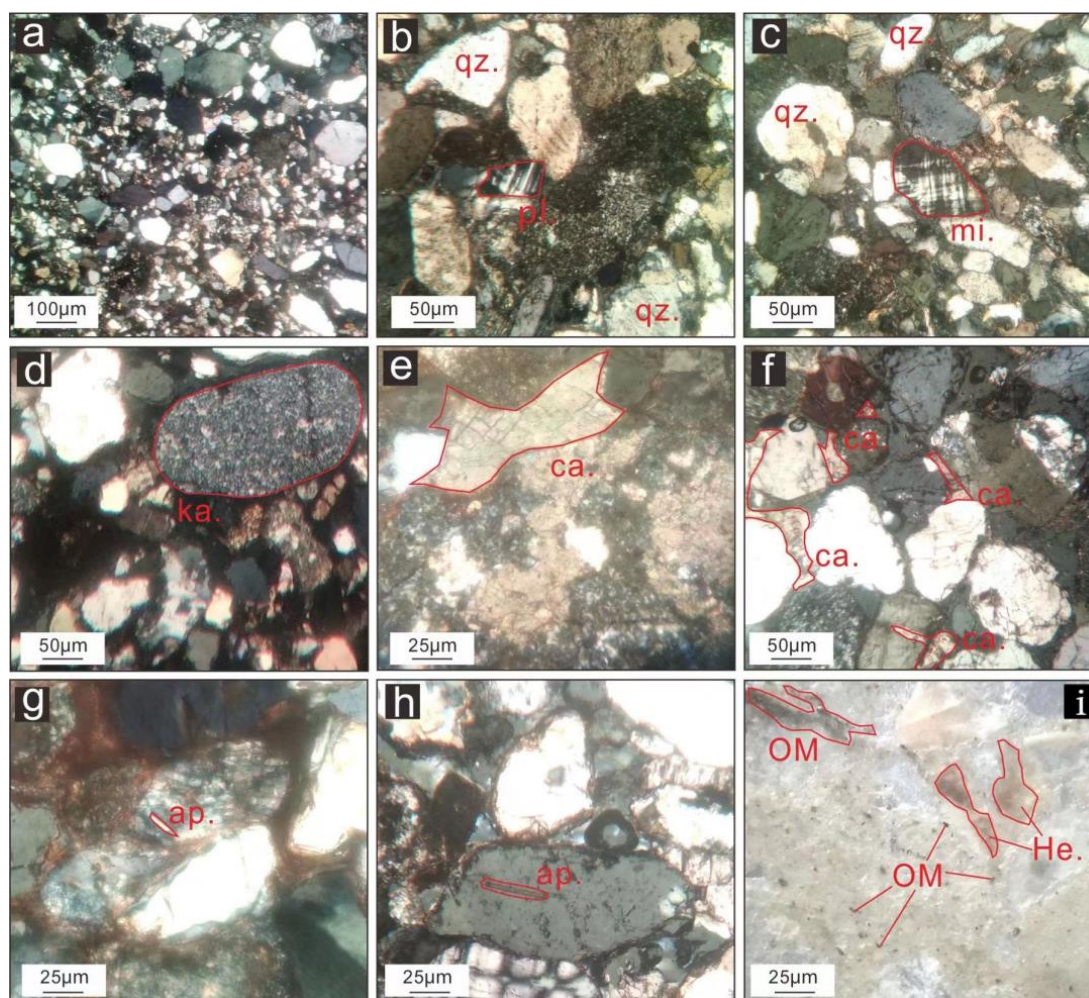


Figure 5. Polarized light micrographs of sandstone samples. Note: qz. = quartz; pl. = plagioclase; mi = microcline; ca. = calcite; ap. = apatite; ka. = kaolinite; He. = hematite; OM = organic matter. (a–c,e–g,i) for fresh sandstone samples. (d,h) for weathered samples.

5. Discussion

5.1. C, N, and P Stoichiometry of Fresh and Weathered Rocks

Rock weathering is a common geological evolution process on the earth's surface. It occurs in the critical zone, where the geosphere, biosphere, hydrosphere, and atmosphere interact with each other, and is an important link in the biogeochemical cycling of elements [32]. As shown in Figures 2 and 3, C concentration was much higher in the fresh sandstone compared with those after weathering ($p < 0.001$). A similar trend was observed in C/N and C/P ($p < 0.001$). However, N, P, and N/P concentrations did not change remarkably before and after weathering. It is clear that weathering significantly reduced rock C concentration (Figures 2 and 3)—namely, the residual C in the weathered rock can be very small, and the high C concentration for some rock weathering products may be caused by other biological processes. During decarbonation, most C from carbonate is lost as CO_2 , and only a part remains as bicarbonate that mostly is dissolved and leached out of the soil. Due to the drastic reduction of the C content in weathered rock, the rock C/N and C/P ratio also decreased sharply by weathering. It was well-proven that carbonate dissolution is fast under acid and humid conditions in the study areas [33]. In addition, the metal elements of carbonates may be retained in soil by the inner- and outer-sphere-exchangeable complex (clays + humus) and can effectively, at least in part, be taken up by microbes and plants.

We found that there was no significant change in N concentration between the fresh rock and weathered rock (Figures 2 and 3). Previous studies stated that bedrock is a

nitrogen source that rivals atmospheric nitrogen inputs across major sectors of the global terrestrial environment [24]. Nitrogen in sedimentary rock exists in two forms: one is in silicate mineral particles and the other is in the form of organic matter in the pores between mineral particles [26]. This study indicated that the organic matter and silicate minerals such as microcline grains were found in the fresh and weathered rocks and that some substantial concentrations of N can exist in these materials. N can be in the form of NH_4^+ and can replace K in microcline [34]. In other words, a lot of rock N will be kept in weathering products and may serve as the original N source of soil [33,35].

Chemical weathering plays a crucial part in the biogeochemical cycle of P [6]. Weathering can produce secondary minerals and liberate plant-essential nutrients into the soil solution. The mineral-derived macronutrients are essential for plants; P is required in the highest concentrations relative to its abundance in the upper continental crust [21], and P is also the most common rock-derived limiting nutrient in terrestrial ecosystems [21,36]. Hahm et al. [21] found that differences in forest cover can be explained by variations in the geochemical composition of bedrock, and bedrock geochemistry is a regulator of vegetation in the Sierra Nevada. Nutrient supply from a regolith depth of several meters is critical for the forest ecosystem function [22]. The forest floor nutrient losses are not necessarily balanced by supply from external atmospheric dust deposition but rather through nutrient uptake from a deep reservoir that is rich in biologically available mineral nutrients—the “geogenic nutrient pathway” [22]. Uhlig et al. [37] also found that P becomes recycled, i.e., remineralized from organic litter and then utilized. Major P inputs are atmospheric deposition and release from rock by chemical weathering. Weathering from rocks is the most important source of P, a study stated that weathering releases 5.5×10^{10} moles of P per year on a global scale [38]. Meybeck [39] also assumed that P is input into the global soil phosphorus reservoir via rock weathering in order to balance outputs from this reservoir. If P removal mechanisms and rates remain approximately constant, increasing atmospheric deposition will enlarge the P pool of the forest ecosystem over decades to centuries [40]. However, our results show that there is no significant difference in P concentration before and after weathering; yet it is interesting that the P concentration of rock slightly increased after rock weathering. One possible explanation is that the dissolved P of parent rocks was subject to incorporation into solid phases of weathered rock [6]. In particular, phosphorus was converted from the dissolved form into organic or particulate inorganic forms and hence fixed in weathered rock [6]. As the leaching rate of apatite is lower compared with other minerals abundant in the studied rocks, such as carbonates, and despite the fact that some P can be released, the rock loses in proportion more of the other elements, and thus P concentration remains stable or even increases despite the potential release of some P. On the other hand, within the weathered rock, the mineral voids (including fissures) were replaced by apatites, which showed significant enrichment of P within weathered minerals [33]. The enrichment of P is more likely due to the transformation of apatite-bound P into more stable secondary P forms [41]. P released from primary apatite can precipitate with dissolved calcium to form secondary apatite, thereby preventing P loss. This slow, effective release from rocks assures a long-time permanence of P in the system. Furthermore, due to the change in N and P concentration, there was no distinct difference in the N/P ratio between fresh and weathered rocks.

5.2. Allometric Relationship of Rock C, N, and P Stoichiometry Response to Weathering

The SMA slopes of the relationship between C and P concentration were statistically different from $|1.00|$, and the steepest slope was in the fresh sandstone. Although there was a positive correlation between C concentration and C/N and C/P ratios in the fresh sandstone ($p < 0.001$), but there was no such pattern in weathered rock, indicating that weathering changed the distribution pattern of rock nutrient concentration. With rocks weathering chemically, the mineral constituents converted to more stable new assemblages, and much of the contained elements were preserved in resistant minerals, partly reallocated into new minerals, or taken into other parts of the weathering profile [33]. These slopes for

the relationships between C concentration and C/N and between C concentration and C/P were nearly equal among the two types of rocks, which indicated that the relationships were stable. The two type rocks had common slopes for the relationship between N concentration and C/N, between N concentration and N/P, between P concentration and N/P, between C/N and C/P, between C/N and N/P, which demonstrated a strong covariant ability. The slopes for the relationship of C concentrations and C/P ratio in weathered rock were significantly greater than those in fresh rocks. The results suggest that rock nutrients showed flexible allometric relationships, and changes in C concentration may result in a larger change in rock stoichiometry in weathered rock than in fresh rocks. This indicated that the rate and type of weathering can vary depending on the stability of the minerals in the regolith and underlying bedrock [33]. The reduction of C concentration in the rock results in great changes in the stoichiometric equilibrium of C with other elements [42]. In a sense, these studies do manifest that the rate of weathering (dissolution) of rock depends on the detailed nature of the mineral itself, e.g., element concentration [43].

5.3. Driving Mechanism of C, N, and P Stoichiometry and Allometric Relationship during Rock Weathering

As shown in Table 1, C-N, C-P, and N-P are not statistically correlated in both fresh and weathered sandstones. These situations are quite different from those in terrestrial soils where C-N, C-P, and N-P show good correlations [44,45]. In the soil system, C, N, and P exist in soil organic matter, plants, microbes, and humus, and even depend on biological factors, such as C fixation by photosynthesis and N fixation by N fixers from atmospheric N₂. While in the sedimentary system, C and N exist in both organic matter and minerals, and P mainly occurs in minerals. For example, C can exist in calcite and dolomite as cement, some organic matter also contains C and N, and P can exist in apatite. In this study, calcite, microcline, organic matter, and apatite were observed in micrographs of sandstones (Figure 5), confirming the existence form of C, N, and P in sandstone.

Compared with the soil ecosystem, the coupling of rock C, N, and P nutrients did not become further strengthened and complex, due to organisms derived from decomposing organic matter or from the direct and indirect activities of soil microbes or plant roots [43]. However, the scaling exponents of C-N, N-P were indistinguishable among the fresh rocks and weathered rocks, with a common slope, which indicated that no significant difference in the change rate of C and N, and N and P in the two rock types. These observations imply that the weathering product formed may be closely associated with the bedrock primary mineral both compositionally and structurally [43]. For similar reasons, Wilson [43] also found that the capillary water may be expected to be close to equilibrium with the primary mineral in micro fissures and narrow solution channels of fresh rock and weathered rock (slightly) at the base of the same lithologic bedrock. The fresh rock was found to have a rapid decrease in C with increasing P than weathered rock—the phenomenon can be attributed to calcite dissolution and resistance of apatite during the weathering process, which is further supported by the microscope evidence that fresh sandstones have calcite cement (Figure 5f), while weathered sandstones contain apatite (Figure 5g).

Our nutrient distribution and driving mechanism results show that C, N, and P in rocks are mainly fixed in minerals and organic matter. The results show that weathering plays an important role in decreasing C concentration, which is related to the dissolution of carbonate and hydration of microplagioclase. They also show no significant differences in N and P concentration between fresh rocks and weathered rocks. Maybe there are two possible reasons: on the one hand, the hydration of microplagioclase may only occur on the mineral surface and thus cannot release a large amount of N; on the other hand, the resistance of apatite and the limited hydration of microplagioclase indicate that pure chemical weathering may not lead to a large amount of N and P inputs. Therefore, weathering mainly changed the rock C, N, and P stoichiometry and allometric relationship through chemical mechanisms.

6. Conclusions

Weathering has an effect on C, N, and P stoichiometry and allometric relationships of sandstones. The C concentration and C/N, C/P of weathered rocks was significantly smaller than the one in fresh rock, which demonstrated that rock C concentration was affected by rock weathering. But the N/P ratio had no obvious change between the fresh rock and weathered rock, due to weathering causing a slight increase in P concentration in the rocks. Our study shows flexible allometric relationships in rocks, which is different from soil systems. Changes in C concentration may result in a larger change in rock stoichiometry in weathered rock than in fresh rocks. The results reveal that the existing form of C, N and P, which mainly occurred in minerals and organic matter, changed through chemical mechanisms during weathering in sandstone. P tends to accumulate during rock leaching due to the transformation of apatite-bound P into more stable secondary P forms. C disappears the fastest because it is an important component of carbonates that are most susceptible to weathering, with N in between the two situations. In conclusion, our measured stoichiometric data and allometric relationships have the potential to reflect homeostatic regulation signals of weathering, and the C, N, and P concentration variation can be used to assess the biogeochemical nutrient cycling from sandstones during weathering. Taken together, we should strengthen the protection and management of sandstones associated with the C, N, and P ecological stoichiometry and their allometric relationships.

Author Contributions: Conceptualization, Y.C., C.X. and J.Q.; methodology, C.X. and J.Q.; investigation, C.X., J.Q. and H.Z.; data curation, J.Q. and H.Z.; writing—original draft preparation, Y.C., C.X. and J.Q.; writing—review and editing, Y.C., C.X., J.Q., J.P., J.S., Q.Z. and B.L. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the National Natural Science Foundation of China (41601008), Special Funding Project of Fujian Provincial Department of Finance (SC-299), Natural Science Foundation of Fujian Province (2018J01737), and Forestry Department of Fujian Province (2021FKJ29). The authors also thank anonymous reviewers for their helpful suggestions. JS and JP were funded by the Spanish Government grant PID2019-110521GB-I00, the Fundación Ramón Areces grant CIVP20A6621, and the Catalan Government grant SGR2017-1005.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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

References

1. Reiners, W.A. Complementary models for ecosystems. *Am. Nat.* **1986**, *127*, 59–73. [[CrossRef](#)]
2. Elser, J.J.; Fagan, W.F.; Denno, R.F.; Dobberfuhl, D.R.; Folarin, A.; Huberty, A.; Interlandi, S.; Kilham, S.S.; McCauley, E.; Schulz, K.L.; et al. Nutritional constraints in terrestrial and freshwater food webs. *Nature* **2000**, *408*, 578–580. [[CrossRef](#)] [[PubMed](#)]
3. Chen, X.L.; Chen, H.Y.H. Plant mixture balances terrestrial ecosystem C:N:P stoichiometry. *Nat. Commun.* **2021**, *12*, 4562. [[CrossRef](#)] [[PubMed](#)]
4. Liu, R.; Zhao, H.; Zhao, X.; Drake, S. Facilitative effects of shrubs in shifting sand on soil macro-faunal community in Horqin Sand Land of Inner Mongolia, Northern China. *Eur. J. Soil Biol.* **2011**, *47*, 316–321. [[CrossRef](#)]
5. Kang, S.W. *Effects of Nitrogen and Phosphorus Addition on Plant Community Structure and Seasonal Dynamics in Typical Grassland of Inner Mongolia*; Inner Mongolia University: Hohhot, China, 2019.
6. Gardner, L.R. The role of rock weathering in the phosphorus budget of terrestrial watersheds. *Biogeochemistry* **1990**, *11*, 97–110. [[CrossRef](#)]
7. Wu, L.J.; Li, X.; Zhao, M.L.; Bai, Y.F. Grazing regulation of phosphorus cycling in grassland ecosystems: Advances and prospects (in Chinese). *China Sci. Bull.* **2020**, *65*, 2469–2482. [[CrossRef](#)]
8. Sinsabaugh, R.L.; Hill, B.H.; Follstad Shah, J.J. Ecoenzymatic stoichiometry of microbial organic nutrient acquisition in soil and sediment. *Nature* **2009**, *462*, 795–798. [[CrossRef](#)]
9. Sterner, R.W.; Elser, J.J. *Ecological Stoichiometry: Biology of Elements from Molecules to the Biosphere*; Princeton University Press: Princeton, NJ, USA, 2002.
10. Li, H.W.; Wang, S.J.; Bai, X.Y.; Cao, Y.; Wu, L.H. Spatiotemporal evolution of carbon sequestration of limestone weathering in China. *Sci. China Earth Sci.* **2019**, *62*, 974–991. [[CrossRef](#)]

11. Sardans, J.; Rivas-Ubach, A.; Peñuelas, J. The elemental stoichiometry of aquatic and terrestrial ecosystems and its relationships with organismic lifestyle and ecosystem structure and function: A review and perspectives. *Biogeochemistry* **2012**, *111*, 1–39. [[CrossRef](#)]
12. Li, J.W.; Liu, Y.L.; Hai, X.Y.; Shangguan, Z.P.; Deng, L. Dynamics of soil microbial C:N:P stoichiometry and its driving mechanisms following natural vegetation restoration after farmland abandonment, *Sci. Total Environ.* **2019**, *693*, 133613. [[CrossRef](#)]
13. Buchkowski, R.W.; Shaw, A.N.; Sihi, D.; Smith, G.R.; Keiser, A.D. Constraining carbon and nutrient flows in soil with ecological stoichiometry. *Front. Ecol. Evol.* **2019**, *7*, 382. [[CrossRef](#)]
14. Doi, H.; Cherif, M.; Iwabuchi, T.; Katano, I.; Stegen, J.C.; Striebel, M. Integrating elements and energy through the metabolic dependencies of gross growth efficiency and the threshold elemental ratio. *Oikos* **2010**, *119*, 752–765. [[CrossRef](#)]
15. Zhao, N.; Yu, G.R. Application of metabolic theory of ecology in global carbon cycle studies. *Quat. Sci.* **2014**, *34*, 891–897.
16. Peñuelas, J.; Fernández-Martínez, M.; Ciais, P.; Jou, D.; Piao, S.; Obersteiner, M.; Vicca, S.; Janssens, I.A.; Sardans, J. The bioelements, the elementome and the “biogeochemical niche”. *Ecology* **2019**, *100*, e02652. [[CrossRef](#)] [[PubMed](#)]
17. Wright, I.J.; Reich, P.B.; Westoby, M.; Ackerly, D.D.; Baruch, Z.; Bongers, F.; Cavender-Bares, J.; Chapin, T.; Cornelissen, J.H.C.; Diemer, M.; et al. The worldwide leaf economics spectrum. *Nature* **2004**, *428*, 821–827. [[CrossRef](#)]
18. Kerkhoff, A.J.; Fagan, W.F.; Elser, J.J.; Enquist, B.J. Phylogenetic and growth form variation in the scaling of nitrogen and phosphorus in the seed plants. *Am. Nat.* **2006**, *168*, 103–122. [[CrossRef](#)]
19. Suchet, A.; Probst, J.L.; Ludwig, W. Worldwide distribution of continental rock lithology: Implications for the atmospheric/soil CO₂ uptake by continental weathering and alkalinity river transport to the oceans. *Glob. Biogeochem. Cycles* **2003**, *17*, 2.
20. Jiang, C.S. *Study on Release Laws of Nutrient during Purple Rock Weathering and the Mechanism of its Fragments Fertilizing*; Southwest University: Chongqing, China, 2001.
21. Hahm, W.J.; Riebe, C.S.; Lukens, C.E.; Araki, S. Bedrock composition regulates mountain ecosystems and landscape evolution. *Proc. Natl. Acad. Sci. USA* **2014**, *111*, 3338–3343. [[CrossRef](#)]
22. Uhlig, D.; Amelung, W.; von Blanckenburg, F. Mineral nutrients sourced in deep regolith sustain long-term nutrition of mountainous temperate forest ecosystems. *Glob. Biogeochem. Cycles* **2020**, *34*, e2019GB006513. [[CrossRef](#)]
23. Morford, S.L.; Houlton, B.Z.; Dahlgren, R.A. Increased forest ecosystem carbon and nitrogen storage from nitrogen rich bedrock. *Nature* **2011**, *477*, 78–81. [[CrossRef](#)]
24. Houlton, B.Z.; Morford, S.L.; Dahlgren, R.A. Convergent evidence for widespread rock nitrogen sources in Earth’s surface environment. *Science* **2018**, *360*, 58–62. [[CrossRef](#)] [[PubMed](#)]
25. Zhang, H.F.; He, G.; Sun, Q.B.; Ji, X.H.; Ouyang, J.P.; He, Z.Y.; Kang, M.R.; Chen, Y. Diversity of dark septate endophytes in cliff-top plant roots in Longhu Mountain, Jiangxi Province, East China. *Mycosystema* **2021**, *40*, 2700–2715.
26. Xu, C.B.; Qiu, J.T.; Zhong, Q.L.; Li, B.Y.; Cheng, D.L.; Zeng, H.Z.; Chang, Y.N.; Yu, H.; Zheng, W.T.; Zou, Y.X.; et al. Reflectance spectroscopy applied in sandstone weathering and nitrogen excretion: A case study in Longhushan Mountain, Jiangxi province. *Spectroscopy Spectr. Anal.* **2019**, *39*, 3801–3808.
27. Liu, X.; Guo, F.S.; Chen, L.Q.; Li, X.M.; Liu, F.J. Lithologic control on the development of Danxia landscapes in red basins. *Mt. Res.* **2019**, *37*, 214–221.
28. Wu, B.J.; Peng, B.; Zhang, K.; Kuang, X.L.; Tu, X.L.; Fang, X.H.; Zeng, D.Z. A new chemical index of identifying the weathering degree of black shales. *Acta Geol. Sin.* **2016**, *90*, 818–832.
29. Chang, Y.N.; Li, B.Y.; Zhong, Q.L.; Wang, G.B.; Shen, Q.S.; Xu, C.B.; Zhang, S.H. Biomass allocation of three functional types of forest tree seedlings and their relationship with nutrients in fine roots and leaves. *Chin. J. Ecol.* **2022**, *41*, 2090–2097.
30. Liu, X.S.; Siemann, E.; Cui, C.; Liu, Y.Q.; Guo, X.M.; Zhang, L. Moso bamboo (*Phyllostachys edulis*) invasion effects on litter, soil and microbial PLFA characteristics depend on sites and invaded forests. *Plant Soil* **2019**, *438*, 85–99. [[CrossRef](#)]
31. Yang, H.S.; Zhang, Q.; Dai, Y.J.; Liu, Q.; Tang, J.J.; Bian, X.M.; Chen, X. Effects of arbuscular mycorrhizal fungi on plant growth depend on root system: A meta-analysis. *Plant Soil* **2015**, *389*, 361–374. [[CrossRef](#)]
32. Hao, L.B.; Dong, J.; Zhao, Y.Y.; Lu, J.L.; Bi, X.G. Geochemical Characteristics of Granite Weathering in central Jilin Province. *J. Jilin Univ. (Earth Sci. Ed.)* **2011**, *41*, 1441–1447.
33. Mcqueen, K.G.; Scott, K.M. Rock weathering and structure of the Regolith. In *Regolith Science*; Scott, K.M., Pain, C.F., Eds.; CSIRO Publishing: Melbourne, Australia, 2008; pp. 103–124.
34. Zhang, Z.H.; Mao, J.W. Ammonium content and nitrogen isotope constraint on metallogenetic and diagenetic environment. *Geol. Rev.* **2002**, *48*, 634–641.
35. Dynarski, K.A.; Morford, S.L.; Mitchell, S.A.; Houlton, B.Z. Bedrock Nitrogen Weathering Stimulates Biological Nitrogen Fixation. *Ecology* **2019**, *100*, e02741. [[CrossRef](#)] [[PubMed](#)]
36. Porder, S.; Vitousek, P.M.; Chadwick, O.A.; Chamberlain, C.P.; Hilley, G.E. Uplift, erosion, and phosphorus limitation in terrestrial ecosystems. *Ecosystems* **2007**, *10*, 158–170. [[CrossRef](#)]
37. Uhlig, D.; Schuessler, J.A.; Bouchez, J.; Dixon, J.L.; von Blanckenburg, F. Quantifying nutrient uptake as driver of rock weathering in forest ecosystems by magnesium stable isotopes. *Biogeosciences* **2017**, *14*, 3111–3128. [[CrossRef](#)]
38. Garrels, R.M.; Mackenzie, F.T.; Hunt, C.A. *Chemical Cycles and the Global Environment*; William Kaufman, Inc.: Los Altos, CA, USA, 1975; p. 206.
39. Meybeck, M. Carbon, nitrogen and phosphorus transport by world rivers. *Am. J. Sci.* **1982**, *282*, 401–450. [[CrossRef](#)]

40. Aciego, S.M.; Riebe, C.S.; Hart, S.C.; Blakowski, M.A.; Carey, C.J.; Aarons, S.M.; Dove, N.C.; Botthoff, J.K.; Sims, K.W.W.; Aronson, E.L. Dust outpaces bedrock in nutrient supply to montane forest ecosystems. *Nat. Commun.* **2017**, *8*, 14800. [[CrossRef](#)] [[PubMed](#)]
41. Walker, T.W.; Syers, J.K. The fate of phosphorus during pedogenesis. *Geoderma* **1976**, *15*, 1–19. [[CrossRef](#)]
42. Sun, H.Y. *Soil Microbial Communities and Its Relationship With Phosphorus along Altitudinal Gradient of Gongga Mountain*; Graduate School of Chinese Academy of Sciences: Beijing, China, 2014.
43. Wilson, M.J. Weathering of the primary rock-forming minerals: Processes, products and rates. *Clay Miner.* **2004**, *39*, 233–266. [[CrossRef](#)]
44. Taylor, P.G.; Townsend, A.R. Stoichiometric control of organic carbon–nitrate relationships from soils to the sea. *Nature* **2010**, *464*, 1178–1181. [[CrossRef](#)]
45. Fan, H.B.; Wu, J.P.; Liu, W.F.; Yuan, Y.H.; Hu, L.; Cai, Q.K. Linkages of plant and soil C:N:P stoichiometry and their relationships to forest growth in subtropical plantations. *Plant Soil* **2015**, *392*, 127–138. [[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.