

Acidic Condition Accelerates Base Cation Release from Purple Rock in Southwestern China

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Abstract

In spite of the fact that rock weathering performs an essential task in the evolution of the Earth's surface, the quantitative assessment between pH and rates of chemical weathering remain unclear. This study aims to characterize the chemical weathering rate of purple rocks (Entisols in USDA Taxonomy) and then develops a model to calculate the release rates of base cations (K^+ , Na^+ , Ca^{2+} and Mg^{2+}) under various pH conditions. Two types of purple rock were sampled from the Shaximiao Group (J_2s) and Penglaizhen Group (J_3p), and a series of laboratory experiments were performed by soaking the purple rocks in solutions with pHs from 2.5 to 7.0, over 24 treatment cycles. The results showed that the release rates of base cations apparently increased as the pH decreased. The release of Ca^{2+} was the dominant process of chemical weathering in J_3p under various pH treatments, while K^+ and Na^+ were remarkably high in J_2s (with the exception of the pH 2.5 treatment).

Quantitative analysis revealed that the rate of cation release was significantly related to the H^+ concentration ($p < 0.001$) and the air temperature ($p < 0.001$). The relationship between cation release and acidity was found to be an exponential function. Our results suggested that solution acidity serves as an important driving force for cation release rates from purple rocks and that environmental acidification would enhance rock weathering.

1. Introduction

Rock weathering can significantly change the physical characteristics of unconsolidated deposit (Birkeland, 1999), and lead to transformation/devastation of the topographies, whilst it can drastically affect the topographic evolution of the tectonic formation of piedmont of mountains (Eppes et al., 2002). As rock weathering represents the initial stage during the development of landforms and the transformation from bedrock to soil, it not only provides a habitat for terrestrial biota but also supplies the cations that determine the long-term availability of plant nutrients (Duan et al., 2002). Additionally, the mineral weathering of bedrock is usually considered to be a crucial stage in the geochemical cycle because it directly affects all terrestrial life (Goldsmith et al., 2010). For example, if the balance between base cation release via chemical weathering and loss through plant uptake is upset, then acidification occurs (Langan et al., 1996; Sverdrup and Warfvinge, 1998). Therefore, the rate of base cations that are released from parent materials through chemical weathering is a critical concern when investigating soil fertility, plant nutrient supply, buffering capacities of soils and surface water quality (Hornung et al., 1990; Langan et al., 1995).

The rate of chemical weathering of rocks is affected by a variety of influencing factors, such as the rock's material properties, topography, climatic conditions (e.g., temperature, precipitation and the chemical composition and pH of rainfall) and biological activity (Nesbitt et al., 1980; Chen et al., 1997; Kirschbaum et al., 2005; Green et al., 2006; Huang et al., 2013). Currently, critical studies have been undertaken on the various factors that impact rock weathering, and it has been recognized that climate factors are most responsible for the weathering rate, in particular temperature and moisture (Warke, 2000). Although a number of investigations have revealed the pH dependence of the slake-durability of rocks (Gupta and Ahmed, 2007; Zhou et al., 2005), the influences of acids on the rate of disintegration as well as chemical weathering of rocks have not been fully investigated. Recently, the combination of acid precipitation (known as 'acid rain') and secondary pollutants (formed through SO_2 , NO_x and NH_3 emissions) has become of an increasing global environmental concern. China has become the third largest global source of acid deposition, following North America and Europe

(Rodhe et al., 2002). Further, acidic rain in both small mountain villages and great cities has been observed, especially in the regions to the south of the Yangtze River, in the basin of Sichuan, and to the east of the Qinghai-Tibet Plateau (Ling et al., 2007). Acidic solutions should exert a strong influence on weathering rates through inputs of H^+ ions, which displace the base cations from their binding sites, limiting their capacity to neutralize acid input and increasing the cation concentration in water (Liu et al., 1990). Related studies have shown that acidic precipitation not only directly accelerates chemical weathering rates through the input of H^+ ions (Huang et al., 2013), but also indirectly drives base cation release through the proton production from nitrogen transformation (Huang et al., 2015). The rate of chemical weathering is therefore crucial to determining whether soils are sensitive to the effects of acid. However, the rate at which base cations are released through rock weathering in acidic environments has always been difficult to measure and quantify because of a variety of environmental factors.

Herein, the considered purple rock is a sedimentary rock, mostly distributed in the southern zone of the Yangtze River and, most commonly, in the Sichuan Basin of Southwest China. These outcrops account for 51.5% of the total area of purple rock distribution in China (He, 2003). Due to its primary characteristic of fast physical weathering, purple rock is easily broken into gravel or fragments of rock by both nature and economic factors, and crops can be planted directly on weathered products. The nutrients within the soils that derive from purple rocks are largely released through the weathering process and especially comprise P- and K-rich minerals; purple rock is generally considered the nutritional base for purple soils (Zhu et al., 1999; He, 2003). Much of the work regarding the study of the physical weathering of purple rock has largely been based on the impacts of moisture and temperature (Zhang et al., 2012; Zhang et al., 2013; Zhang et al., 2015; Zhang et al., 2017). However, the effect of variations in pH on chemical weathering is not yet clear, and other environmental factors may also play a role, making it difficult to predict weathering characteristics under acidic conditions. Therefore, in this study, we aim to determine the quantitative effects of varying acidic solutions on rock decay (weathering) when it is applied to purple rock by using controlled laboratory experiments.

2. Materials And Methods

2.1. Materials

The samples of fresh purple rocks utilized in the experimental measurements were chosen from purple and red-brown mudstones of the group of the Shaximiao Group (J_2s) ($E104^{\circ}51'$, $N29^{\circ}44'$), and the purple and brown sandy mudstone of the Penglaizhen Group (J_3p) ($E105^{\circ}23'$, $N30^{\circ}6'$) in Sichuan Basin, all laid down in the Jurassic period. Sichuan Basin possesses a subtropical, monsoon climate with a yearly mean temperature between 14 and 19 °C and average yearly precipitation of around 850 mm. Most of the precipitation occurs between May and October. To better reflect the authenticity of weathering characteristics in an acidic environment, the fresh purple rock samples without acid effects were selected. Then, all of the samples were taken and treated at the Field Observation and Science Research National Station of Farmland Ecosystem in Yanting, Sichuan of China ($N31^{\circ}16'$, $E105^{\circ}27'$). The clay mineral content of the tested samples (Table 1) was determined using the X-ray diffraction method (Zhang and Fan, 2003). The elements K, Na, Ca and Mg (Table 2) were determined by atomic absorption spectrophotometry. Si, Al, Fe and Ti were using the gravimetric-molybdenum blue photometric method, the fluoride replacement method, the dichromate volumetric method, and the hydrogen peroxide photometric method, respectively (Ministry of Geology and Resources, 2002).

About 58% of precipitation in southwestern China has a pH value between 4.5 and 5.6 (Zhou et al., 2017). The outcomes of acidic rain surveyed by the Sichuan Meteorological Bureau of Dazhou, Xichang, Chengdu, Panzhihua, E'meishan, and Anyue from 2006 to 2013 demonstrated that in Sichuan province, the average frequencies of stronger acids ($\text{pH} \leq 4.0$) are about 17% and the average pH of precipitation is about 4.74 (Zhao et al., 2015). Moreover, it has been detected that the pH value of precipitation in some regions of the Sichuan Basin was very low and ranged from 3.0-3.5 (Wang and Han, 2011; Zhao et al., 2013), and the nitric acid and sulfuric acid were the fundamental resources of acidity within the precipitation. The molar ratio of SO_4^{2-} to NO_3^- is around 4:1 (Zhang et al., 2010; Yang et al., 2014). On the basis of this range, a mixture of synthetic acid solutions comprising H_2SO_4 and HNO_3 with a ratio of the molar concentrations of around 4:1 was prepared. However, a pH lower than 3.0 is unusual in natural environments, the outcomes of acidity on chemical weathering are relatively long procedures, and in the simulation assessment, a lower pH is frequently utilized to simulate the long-lasting impacts of an acidic media within the natural environments for diminishing the involvement of humidity, temperature, and other external parameters (Liu et al., 2010). Hence, the preparation of acidic solutions with values of pH of 5.6, 4.5, 3.5, and 2.5 was carried out through dilution of the stock solution by utilizing deionized water. In these experiments, the deionized water (with a pH of 7.0) was utilized as a control (CK).

2.2. Experimental procedure

To ensure homogeneity, the samples for each treatment were selected from the same block of purple rock. Cut the parent rock sample into small pieces, and each cube was then shaped into a rough sphere with a mass of 660 ± 3 g. All of the tests were conducted in triplicate with the following detailed procedure.

All the prepared experimental samples were randomly placed into 500ml glass beaker. Then, add 300ml of acid solution to each beaker, and it was ensured that all the samples were submerged. After soaking for 72 hours, each solution was filtered and collected to determine the base ion (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) concentration in solution. Put the residual rock cuttings on the filter paper back into the beaker and dried for more than 24 hours at 105°C to a constant weight. All of these decayed products were prepared for the next acid solution treatment after cooling, this procedure represented one treatment cycle. Particles of weathered products less than 2 mm in diameter are commonly regarded as soil particles (Zhu et al., 1999; He, 2003). Therefore, a total of 24 cycles were carried out for all of the treatments because the disintegration rate of the purple rock treated with each acid solution were exceed 90%, which indicated that the disintegration process has basically stopped. Herein, the pH of the collected filtered solutions was determined by a PHS-3E acidimeter, and ion chromatography was used to determine Na^+ , K^+ , Ca^{2+} and Mg^{2+} in the filtered solution.

2.3. Calculation of cation release in the treatment cycle

Based on the solution volume and the ions collected in each soaking test, the amount of K^+ , Na^+ , Ca^{2+} and Mg^{2+} in the filtered solution were calculated in accordance with the following equation [1]:

$$S_i = C_i \cdot V_i / (M_i \cdot m \cdot 1000) \quad [1]$$

where S_i represents the released amounts of K^+ , Na^+ , Ca^{2+} and Mg^{2+} during each treatment cycle ($mmol\ kg^{-1}$); i is K^+ , Na^+ , Ca^{2+} and Mg^{2+} ; C_i is the concentration of each cation in the filtered solution (ppm); V_i represents the volume of filtered solution collected after each soaking (ml); M_i is the relative atomic mass of each atom (K-39, Na-23, Ca-40 and Mg-24) and m indicates the weight of the soaked rock (kg).

As a result, the release rate of base cations is expressed by equation [2]:

$$V_T = \sum S_{i(i=K^+, Na^+, Ca^{2+}, Mg^{2+})} / t \quad [2]$$

where V_T is the total release rate of the base cations K^+ , Na^+ , Ca^{2+} and Mg^{2+} in each treatment cycle ($mmol\ kg^{-1}\ h^{-1}$) and t is the duration time of each soaking (h).

2.4. Data analysis and statistics

Multiple comparisons are used to analyze the effects of different treatments and parent rock types on the amounts of cation release. Analyses of the least significant difference (LSD) tests were performed using the SPSS v.12.0 software to determine whether the amounts of cations released were significantly different for the various acid treatments. After regression analysis, the models of the relationship between the variables were set up via the regressive determination parameters compared by the ORIGIN v.8.0 software. The statistically significant level was set at $p < 0.05$, and the statistical parameters for all of the data were then analyzed using SPSS v.12.0.

3. Result

3.1. Release of cations in the soaking solution

The variation trend of cations in the soaking solution of parent rocks under different acid treatments is similar, that was, the stronger the acid treatment accompanied with the higher the release amount of each cation (Fig. 1). During the whole soaking process, the release amount of each cation under pH 2.5 treatment was significantly greater than that under other acid treatments. The K^+ release process of the two groups of parent rocks under pH 2.5 immersion showed a single peak curve, and obvious peaks appeared in the middle stage of immersion, with the release amounts of 0.037mmol/kg and 0.038mmol/kg from J_2s and J_3p respectively, and then showed a fluctuating downward trend to tend to be stable. The released K^+ of J_2s under pH 3.5, pH 4.5, pH 5.6 and CK treatments were relatively gentle, with little fluctuation and unobvious peak value. However, the K^+ release from J_3p showed two obvious peaks during soaking between pH 3.5 ~ pH 7.0, and the release showed a slow downward trend after the second peak change. The release laws of Na^+ between two parent rocks were basically similar, that the overall trend was fluctuating and declining with the soaking process. Na^+ release of J_3p under different pH acid solution treatment had obvious fluctuation peak in the middle stage of immersion, while it decreased continuously from the beginning of soaking in the J_2s . Na^+ increased slightly under pH 2.5 treatment in the later stage of soaking, while under other pH treatment Na^+ release decreased slowly and the curve changed gently. The Ca^{2+} release curves of J_2s and J_3p in strong acid (pH = 2.5) solution were similar, which had a single peak curve trend, and arrived the peak value of 0.912mmol/kg and 1.417mmol/kg

respectively at the 10th immersion. The Ca^{2+} release laws of J_2s under pH 3.5 to pH 7.0 were similar to that under the treatment of strong acid solution with pH 2.5, and a relative high peak appears in the middle stage of soaking, and then had a fluctuating downward trend. However, the Ca^{2+} release curves of J_3p under the treatment of acid solution with pH value of 3.5 ~ 7.0 were consistent, and the Ca^{2+} release amount were relatively high at the beginning of soaking. With the soaking cycle, the Ca^{2+} release curve fluctuated and the decline range was large at the beginning stage, and it decreased slowly or tends to be gentle at the later stage. The release law of Mg^{2+} under different acid treatments were similar to that of Na^+ . With the progress of soaking process, the overall trend of Mg^{2+} were fluctuating and declining, and the release of Mg^{2+} rapidly decreases to a relatively low value during the middle stage of soaking.

3.2. The effect of pH on the amount of cations released

The amounts of elements released by weathering (the unit charge of elements released from 1 kg of soil during the weathering process) were utilized as a criterion to assess the rate of weathering (Qiu and Yang, 1998). In this study, the amounts of K^+ , Na^+ , Ca^{2+} and Mg^{2+} released from J_3p and J_2s under the effects acid solutions were obvious after 24 treatment cycles. As Table 3 showed, the acid solutions caused more cations to be released than the deionized water for the two rock types. The whole amount of cations released from all of the studied types of rocks enhanced as pH diminished, particularly when pH was less than 3.5, and a significant difference ($p < 0.05$) was observed after the acid treatments. Compared with the control treatment of pH 7.0 (CK), the amount of cations released from sample J_3p after treatment with solutions of pH 2.5, 3.5, 4.5 and 5.6 increased by multiples of 6.50, 1.55, 1.25 and 1.14 times, respectively. Comparable values were 8.23, 1.74, 1.41 and 1.22 times for J_2s . Compared to the CK, the Ca^{2+} released from the pH 2.5 solution apparently increased by 19.59 and 9.59 mmol kg^{-1} for J_3p and J_2s , respectively, and Mg^{2+} increased by 1.20 and 5.82 mmol kg^{-1} . Compared with monovalent cation species, the H^+ concentrations, to a large degree, restricted the release of Ca^{2+} and Mg^{2+} when the pH of the applied solution was lower than 3.5. The release of base cations showed a certain relationship with the composition of the minerals. Ca^{2+} was the predominant cation released under the various acid solutions, with the average Ca^{2+} amount accounting for 49.80% for the two rock types, while Na^+ represented 33.14%, Mg^{2+} 10.96% and K^+ 6.09%.

3.3. Relationship between the amount of cations released and pH

The tendency for specific cations to be released under different acidic solutions was similar for the two rock groups. Regression analysis showed that the amount of released individual cations appeared to exponentially decrease as pH increased in all two of the rock types tested. The exponential correlations between pH and cation release were significant ($p < 0.001$), especially for the amount of Ca^{2+} and Mg^{2+} released, with correlation coefficients (R^2) above 0.999 (Fig. 2). This also illustrated that the sensitivity of cation release to pH variation for the various cation types was high for all two rock types and that Ca^{2+} and Mg^{2+} were more apparent than K^+

and Na⁺. On the whole, these data fit the proposed model and were able to correctly and quantitatively predict the cation amounts released from purple rock under varying acidic environmental conditions in the laboratory.

3.4. Determination of the quantitative relationship between cation release rates and H⁺ concentrations

Intuitively, it can be expected that acid would exert a strong influence on chemical weathering; however, this effect may vary with environmental changes such as air temperature. Many researchers (Yang and Brantley, 1997; Gislason and Oelkers, 2003; Gudbrandsson et al., 2011) have studied the effects of pH and temperature on mineral dissolution kinetics. Previous studies indicated that the rate of water exchange around an octahedral cation can be correlated to the mineral dissolution rates in orthosilicates (Casey and Westrich, 1992). In general, the net total output of base cations (K⁺, Na⁺, Ca²⁺ and Mg²⁺) is used to represent 'chemical weathering' (Paces, 1986); therefore, to provide credible estimates, the chemical weathering rate in acidic environments should be considered and incorporated into future models. To effectively describe the reaction of rock to acidic experimental environments in the laboratory, a total of 120 sets (24 cycles of five treatments) of data were analyzed, including chemical weathering rates, H⁺ concentration of the soaking solution and natural temperature (Fig. 3). Using nonlinear, multivariate regression, Eq. (3) was formulated :

$$V_T = e^{ac(H^+)} \cdot \left(\frac{A}{RT}\right)^\beta \quad [3]$$

where V_T is the same as in equation [2], $c(H^+)$ is the concentration of H⁺ (mmol L⁻¹), T is temperature (K) (Fig. 3), R is the gas constant (kJ mol⁻¹ K⁻¹) and a , β and A are constants to be determined by regression analysis and are dependent on rock material properties.

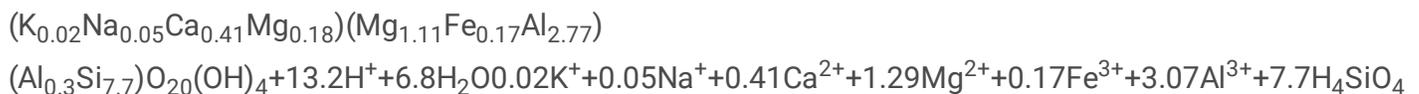
In this study, the chemical weathering rate of base cations was calculated and combined with other variables in equation [3] using SPSS v.12.0, and the results showed that the data fit the model to a significant degree ($p < 0.001$). The correlation coefficients of the cation release rates related to the concentrations of H⁺ were 0.897 and 0.767 for J_{3p} and J_{2s}, respectively, and they were apparently greater than those related to temperature, which were 0.045 and 0.116 for J_{3p} and J_{2s}, respectively. The multiple correlation coefficients (R^2) were above 0.883 and were higher than the partial correlation coefficients (Table 4). Thus, our results showed that the model of chemical weathering rates was not satisfactory when the rate was determined only based on solution acidity (pH) without consideration of the temperature effects.

4. Discussion

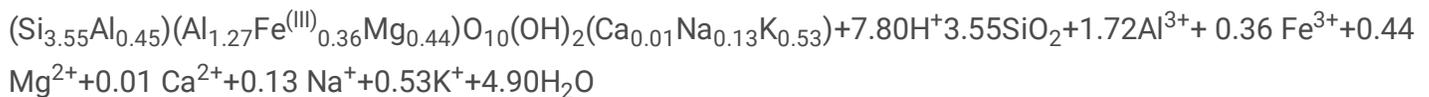
A remarkable number of laboratory investigations have illustrated the essential role of pH in the processes of chemical weathering (Schnoor, 1990; Guicharnaud and Paton, 2006). In this study, our results indicates that the concentration of H⁺ in the reaction environment is an important impact factor for weathering kinetics, consistent with those of previous studies (Huang et al., 2013; Wu et al., 1998; Zhang et al., 2007; Probst et al., 1992). The rate of the release of cations from the purple rocks obviously enhanced as the solution pH diminished, especially when the value of pH was less than 3.5 (Table 3). Similarly, the effect of acidification on

chemical weathering is low (Sverdrup and Warfvinge, 1995), therefore, long-term evaluation is necessary to reveal the effects of acid deposition on chemical weathering (Probst et al., 1992). However, a pH less than 3.5 is infrequent in natural environments, the impacts of acidity on chemical weathering involve the relatively long procedures, and in simulation assessments, a lesser pH is commonly utilized to stimulate the long-lasting impacts of acidic media in nature to diminish the involvement of humidity, temperature, and other external parameters (Liu et al., 2010). In the current research, the performed analysis of cation release divulged substantial impacts of pH on chemical weathering among the two purple rocks, particularly when the amount of Mg^{2+} and Ca^{2+} released during the pH 2.5 processing was considered. The effects were significantly greater than those caused by the other treatments, which was attributed to the fact that compared to univalent cations, the divalent cations released were more affected by the pH of the environment (Liu et al., 1990; Hartikainen, 1996). Calcium in the rock mainly exists in inorganic form, and inorganic calcium can be further divided into mineral and exchange state calcium (Yuan, 1983). Of these, mineral calcium mainly exists in the crystal lattice of the rock in its solid phase and can seldom be released through hydrolysis. In contrast, the calcium-bearing minerals in purple rock are mainly silicate minerals and carbonate minerals. The acidities of silicic acid and carbonic acid are weaker than those of the simulated solutions due to the action of mixed acids of SO_4^{2-} and NO_3^- . In this way, the calcium within silicate and carbonate minerals can be easily dissolved by acid. In contrast, the released quantity of potassium is evidently lower than that of calcium, which is mainly because most of the calcium-bearing primary minerals in the rock are easily weathered. In particular, the weathering rate of calcium-bearing plagioclase is much higher than that of potassium feldspar or sodic feldspar (Yuan, 1983). Meanwhile, the lattice energy of calcium-bearing minerals is much smaller than those of sodium- or potassium-containing minerals of the same type (Yuan, 1983). Additionally, the major clay minerals of the purple block (including illite, montmorillonite, and chlorite) are all phyllosilicate-based minerals with a ratio of 1:2 in illite and montmorillonite and in chlorite a ratio of 2:1:1 (Verburg and Baveye, 1994). The reactions of these minerals in acidic solutions may be represented as follows:

Montmorillonite (Amram and Ganor, 2002):



Illite (Vieillard, 2000):



Chlorite (Tang et al., 2007):



These reactions promoted the replacement of intercrystalline Ca^{2+} , Mg^{2+} , Fe^{3+} and Na^+ by H^+ in the solution. However, the crystal structure of illite, which accounts for the vast majority of the clay mineral composition of the rock, constitutes two tetrahedral sheets with face-to-face top oxygen molecules. Moreover, the layers are tightly stacked in a staggered arrangement, and a coordinate, co-edge, octahedral combination is produced by

the superposition, forming an octahedral sheet (O). Thus, a basic structural layer is formed, the interlayer space of which is filled with K^+ with an equilibrium electrovalence. The K^+ exposed between the layers is directly absorbed onto the silica tetrahedra and is not easily replaced by H^+ in the solution.

On the basis of transition state theory, chemical weathering processes may be influenced by the proton or aqueous activities of elements (Zhu et al., 2013). The distribution of cations (K^+ , Na^+ , Ca^{2+} and Mg^{2+}) on the ternary diagrams presented in Fig. 4 can be used to indicate the relative contributions of major ions under various acidic environments (Huh, 2003). Silicate- and carbonate-rich minerals are major components of the purple rock lithologies; therefore, considering that they can be weathered easily (especially carbonates), they are expected to contribute significantly to the major cation budget of the chemical weathering process (Zhu et al., 2013). Therefore, Ca^{2+} was the dominant species in J_{3p} under various acid treatments, while K^+ and Na^+ were remarkably high in J_{2s} except for the pH 2.5 treatments. Notably, the relative contributions of major cations to chemical weathering varied with pH and time. The proportion of Ca^{2+} released by $pH \geq 3.5$ treatments was substantially decreased when compared with the Ca^{2+} released by the treatment at pH 2.5. The proportions of Na^+ and K^+ behaved in the opposite manner, and the contribution rate of Mg^{2+} changed only slightly with changing pH. On average, the release of Mg^{2+} only accounted for a small fraction of the major cations, and its contribution in J_{3p} approached 0 with an increase in time; it should also be noted that the contributions of Na^+ and K^+ increased.

The rate of chemical weathering is usually quantified by measuring solute concentrations and flux (Drever and Zobrist, 1992; Stonestrom et al., 1998). Past research has focused on the effects of changing temperature and reactive fluid composition on the chemical rates of individual minerals in the laboratory (Oelkers and Schott, 2001; Schott et al., 2009). However, natural rocks consist of many different minerals with distinct reactive and surface areas; thus, different rocks have distinct responses to pH and temperature. Concerning the constituents of its materials, purple rocks include a considerable percentage of clay minerals, namely, illite, montmorillonite, chlorite, and so forth. According to studies of influence factors on clay mineral weathering, the clay mineral dissolution rates increase with temperature strongly depends on pH (Huertas et al., 2001; Köhler et al., 2003), and previous investigations have exhibited that more quickly dissolution could be achieved by a departure from neutral pH circumstances. Furthermore, at greater temperatures, the rate of solution is greater (Oelkers et al., 2008; Bray et al., 2015). A thorough study on phyllosilicate weathering indicates that the rate of weathering is lesser at low temperatures and moderately acidic to neutral pH, and it is greater at higher temperatures and lower pH, which are divided through a transition zone (Lamarca-Irisarri, et al., 2019). Regression analysis of our results revealed that the relationships between cation release rate, H^+ concentration and natural temperature were significant for the tw purple rock samples ($p < 0.001$). According to partial correlation coefficients (Table 4), both the H^+ concentration and temperature significantly influenced the cation release rates ($p < 0.001$). Temperature affected not only the absorption of protons on the surface (Cama et al., 2002) but also the physical erosion of purple rock (Zhang et al., 2015). Previous researchers have indicated a positive relationship between chemical and physical weathering rates (Riebe et al., 2003; Singh et al., 2005). Therefore, any attempts to model cation release rates based on the independent effect of pH alone and without consideration of temperature effects will be unsatisfactory; our developed model (equation [3]) would be more accurate for the prediction of cation release rates under environments with variable acidity.

5. Conclusion

Our results show that the total amount of base cations (K^+ , Na^+ , Ca^{2+} , and Mg^{2+}) released from purple rock during the chemical weathering process significantly ($P < 0.001$) increases with an increase in H^+ concentration. The release of Ca^{2+} is the main contribution to cation release from the J_{3p} under various acid treatments, while K^+ and Na^+ are the main cations released from the J_{2s} , with the exception of the pH 2.5 treatment. The models for cation release rates fit the observed data well when the two variables are introduced (i.e., H^+ concentration and air temperature), and there is a significant ($P < 0.01$) exponential relationship between the amount of cations released and the pH. Therefore, these models can be considered to be a baseline that will allow the base cation release rates of purple rock to be quantitatively predicted under varying environmental acidification conditions. In conclusion, our results suggest that acidity is a critical driving force in the chemical weathering of purple rock.

Declarations

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Data Availability

All the data generated and provided in the study is included under the main article and supplementary material file.

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Tables

Table 1 Mineral contents (%) of the two purple mudstones

Rock types	Montmorillonite	Illite	Kaolinite	Chlorite	Quartz	Potassium feldspar	Plagioclase	Calcite	Dolomite
J ₂ s	13	21	6	7	41	2	10	0	0
J ₃ p	5	23	0	11	38	1	8	12	2

Table 2 Major chemical element contents (%) of the two purple mudstones

Rock types	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	CaO	MgO	CaCO ₃
J ₂ s	61.51	16.21	6.55	0.78	2.59	1.29	0.86	2.04	2.15
J ₃ p	58.26	13.03	4.68	0.64	2.43	0.87	5.01	1.25	14.65

Table 3 Amounts of cations released from purple rock under various pH weathering conditions

Rock types	pH	Amount of cations released (mmol kg ⁻¹)			
		K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺
J ₂ s	2.5	0.61±0.03a	3.19 ±0.21a	10.43±0.20a	6.12±0.05a
	3.5	0.29±0.02b	2.09±0.13b	1.30±0.03b	0.62±0.03b
	4.5	0.26±0.01c	1.78±0.14c	1.05±0.05c	0.39±0.02c
	5.6	0.20±0.01d	1.49±0.14d	0.97±0.03c	0.36±0.01c
	CK	0.18±0.01de	1.15±0.07e	0.84±0.02d	0.30±0.02d
J ₃ p	2.5	0.76±0.02a	2.37±0.28a	22.08±0.25a	1.46±0.05a
	3.5	0.40±0.01b	1.77±0.17b	3.82±0.05b	0.35±0.01b
	4.5	0.33±0.01c	1.49±0.14bc	2.97±0.02c	0.32±0.01bc
	5.6	0.32±0.04c	1.33±0.15cd	2.72±0.03d	0.29±0.01cd
	CK	0.30±0.03c	1.05±0.11e	2.49±0.05e	0.26±0.01e

Note: Different letters in a column indicate significant differences between the treatments, where $P < 0.05$.

Table 4 Quantitative model of cation release rates for the two groups of rock

Rock groups	Regression equations	Correlation coefficients (R^2)	Partial correlation coefficients ($R_{c(H^+)}^2, R_T^2$)		p
J ₂ s	$v_T = e^{0.61 \cdot c_{(H^+)}} \cdot \left(\frac{3853.10}{RT}\right)^{-14.02}$	0.883	0.767	0.116	<0.001
J ₃ p	$v_T = e^{0.56 \cdot c_{(H^+)}} \cdot \left(\frac{5472.96}{RT}\right)^{-7.34}$	0.942	0.897	0.045	<0.001

Figures

Figure 1

Cations released in the soaking solution from J₂s (a) and J₃p (b) after each treatment cycle. Note: The inserts in Fig.1 show enlargements of the parts of released Ca²⁺ and Mg²⁺ with the pHs of 3.5, 4.5, 5.6 and CK.

Figure 2

Relationship between the total cations (K⁺, Na⁺, Ca²⁺ and Mg²⁺) released and pH

Figure 3

Average air temperature during each soaking treatment

Figure 4

Ternary diagrams showing the cation compositions of purple rocks J₃p (a) and J₂s (b) from the filtered solutions used in the present study

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