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Original Research

Exploration of the Enrichment Process of Heavy Metal Elements in Carbonate Rocks Weathered Soil: Insights from Acid Leaching Experiments

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Abstract

Significant enrichment of heavy metal elements occurs during the process of carbonate rocks weathering into the soil, but the factors contributing to this enrichment are not yet fully understood. This study compared the variations in heavy metal elements (Cr, Ni, Cu, Zn, Cd, and Pb) concentrations between carbonate rocks and clastic rocks, as well as their weathered soils. The findings indicate that, under the driving forces of different weathering patterns, the geochemical behavior of heavy metal elements exhibits significant differences. The enrichment and accumulation of heavy metal elements in carbonate weathered soils can be attributed to the absolute loss of mass and relative enrichment in terms of concentrations. This study further investigated the role of acid-insoluble residues in influencing the characteristics of mineral phase and migration enrichment degree of heavy metal elements in carbonate rocks through acid leaching experiments. The results demonstrate that heavy metal elements are generally inclined to be present in acid-soluble mineral phases and exhibit a distribution pattern where higher levels of acid-insoluble residues correspond to a greater tendency for heavy metal elements to be enriched in the acid-insoluble mineral phase. The migration and enrichment degree of heavy metal elements in the weathered soils of carboniferous and Permian carbonate rocks in the study area are significantly higher than those in the Cambrian system. This indicates that lower levels of acid-insoluble residues correspondingly result in more intense leaching during their weathering process. Furthermore, the concentration of heavy metal elements in the acid-insoluble residues of carbonate rocks to some extent controls the characteristics of heavy metal elements content in weathered soils. This is an important factor leading to variations in the enrichment degree of heavy metal elements in carbonate weathered soils across different geological epochs. This study provides new insights into the factors contributing to the enrichment of heavy metal elements in carbonate weathered soils. Considering the unique weathering patterns of carbonate rocks, it is recommended to prioritize the monitoring of heavy metal elements concentrations in overlying soils, surface runoff, and karst groundwater in the study area.

Keywords: soil heavy metal, carbonate rocks, acid-insoluble residues, leaching experiments

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Introduction

The pedosphere is an essential sphere within the Earth's critical zone, and there exists a synergistic relationship between soil quality and the regional ecological environment [1, 2]. The soil environment, as the most active geochemical system for element migration and material cycling in nature, is highly susceptible to various pollution sources [3-6]. It is generally believed that the enrichment and accumulation of heavy metal elements in the soil are the combined result of anthropogenic activities and the release from the weathering of parent rocks [7-9]. In industrial areas, agricultural regions, and urban residential areas, human activities predominantly contribute to heavy metal pollution [10-13]. However, in underdeveloped regions and remote mountainous areas, the accumulation of heavy metal elements in the soil is primarily influenced by regional geological background factors [14-18].

The southwestern region of China is the largest karst distribution area in the world [19] and also an area with geochemical anomalies of multiple metal elements [20-22]. The regional geochemical survey conducted in China during the 1980s at a scale of 1:200,000 indicated that the concentrations of various heavy metal elements in soil and sediments in the southwestern region of China were higher than the background values of soil elements in China [23, 24]. Numerous studies have confirmed that the weathering of carbonate rocks results in significant enrichment of heavy metal elements in soils. This is considered the main reason for the widespread exceedance of soil heavy metal element concentrations in the karst regions of southwestern China [25-27]. In previous studies, researchers have conducted extensive work on spatial distribution characteristics [28-30], environmental risk assessment [31-33], pollution source analysis [34-36], and other aspects of heavy metal elements in karst regions. However, there is no definitive conclusion regarding the exact causes of excessive enrichment of soil heavy metal element concentrations. Current research generally suggests that the weathering of carbonate rocks into soil involves significant dissolution of carbonate minerals, leading to the enrichment of trace metal elements in the residual insoluble residues [37, 38]. If that is the case, under conditions without external input of heavy metals, the concentration of heavy metal elements in both carbonate rock bedrock and soil should exhibit a positive correlation. However, the extensive leaching of carbonate minerals often results in the loss of elemental geochemical information between the carbonate rock parent material and the soil [39], making it difficult to discuss the enrichment mechanism of soil heavy metal elements from the perspective of parent rocks. Additionally, despite being weathering products derived from the same parent rock (carbonate rock), variations in mineral composition can result in different degrees of geochemical behavior of heavy metal elements during the weathering process [40]. Existing studies have confirmed that the overlying soil in karst areas is a product of in situ weathering residues of acid-insoluble constituents in the underlying bedrock [41, 42]. Therefore, it is reasonable and feasible to utilize the acid-insoluble fraction of carbonate rocks as a 'bridge' to understand the elemental geochemical information between the rock-to-soil weathering sequence.

This study focuses on the enrichment mechanisms of heavy metal elements in weathered soils derived from carbonate rocks. By comparing the geochemical behavior of heavy metal elements under natural weathering conditions between carbonate rocks and clastic rock profiles in the study area and conducting acid-insoluble fraction extraction experiments on carbonate rocks, we further investigate the role of acid-insoluble fraction in influencing the mineralogical occurrence and migration extent of heavy metal elements. This study can not only deepen our understanding of the geochemical behavior of heavy metal elements in karst regions but also provide a scientific reference for regional soil heavy metal pollution prevention and control.

Materials and methods

Study area

The study area is located in Guizhou Province, southwestern China, between E103°36'~109°35' and N24°37'~29°13' (Fig. 1). It has a subtropical humid monsoon climate with an annual precipitation of approximately 1100~1400 mm and an average annual temperature ranging from 16 to 18°C. During the Ordovician and Triassic periods, Guizhou Province was predominantly submerged in a marine depositional environment, leading to the extensive development of marine carbonate rock formations. These formations account for approximately 61.9% of the total area of Guizhou Province, with the Cambrian, Carboniferous, and Permian series being the most typical [43]. The widespread occurrence of carbonate rocks provides the material basis for the development of karst landforms in the study area, while also serving as an ideal research 'window' to reveal the geochemical behavior of heavy metals elements in weathered soils derived from carbonate rocks. The parent rocks in the study area are mainly composed of carbonate rocks, with a small amount of clastic rocks, basalt, and granite. The dominant soil types include lime soil and zonal yellow soil.

Sampling, Preparation, and Testing Methods

Sample Collection

The main objective of this study is to investigate the geochemical behavior of heavy metal elements under natural weathering conditions. Therefore, it is crucial to determine whether the collected samples can objectively reflect the natural background values of these elements. To avoid excessive human impact on the content of heavy metal elements in soils, the selected profile locations for this study were all situated in the southern region of Guizhou Province (Fig. 1). In comparison to other regions within the province, this area has a relatively lower population density and fewer industrial and mining enterprises. Moreover, each profile is located in areas far from human activities (> 500m) without any traces of accumulated profiles.

This study collected rock and soil samples from the underlying bedrock and overlying weathered soils of different stratigraphic formations (Cambrian, Carboniferous, and Permian) in the study area. A total of 20 rock samples (15 carbonate rocks and 5 clastic rocks) and 92 soil samples (60 carbonate rocks and 32 clastic rocks) were collected. During fieldwork, fresh rock fragments were collected as much as possible for the bedrock samples, while soil samples were obtained by trenching from bottom to top. The collected samples were sealed in self-sealing bags for preservation and transported to the laboratory for further processing. Rock samples were washed with an ethanol solution to remove surface impurities, while soil samples were carefully cleaned to eliminate plant roots and gravel mixed within. After the samples were air-dried naturally, they were ground in an agate mortar to pass through a 200-mesh sieve and then stored in bags for further use.

Microscopic Rock Identification

This study selected representative carbonate rock samples, which were cut into quadrangular, thin sections using a cutting machine. After washing, the sections were wiped clean with a silk cloth and then air-dried. A suitable amount of neutral gum solution was dropped onto the sections to create thin slides placed on glass slides. The positioning of the glass slides was adjusted using stainless steel tweezers to ensure a thin, uniform, secure, and bubble-free adhesive layer, facilitating microscopic observation.

Preparation of Acid-Insoluble Residue

In this study, an appropriate amount of carbonate rock samples were taken and subjected to crushing. The crushed samples were then placed into a 1L beaker, followed by a gradual addition of 1M HCl for reaction. Once the reaction inside the beaker ceased, the supernatant liquid was removed using a siphoning pipette, and additional HCl was added. This process was repeated until no further reaction occurred (indicating the endpoint of the reaction). Subsequently, the solid residue (insoluble residue) in the beaker was thoroughly rinsed with ultrapure water. After confirming the neutrality of the supernatant liquid using pH test paper, the insoluble residue in the beaker was transferred, dried, weighed, and stored in a bag for further use. This study prepared a total of 15 samples of insoluble residues from car bonate rocks using the aforementioned method.

Trace Element Testing of Samples

The rock, soil, and insoluble residue samples were weighed using an analytical balance, with 50mg placed into PTFE digestion vials. Then, 1mL of concentrated HNO_3 and 0.6 to 0.8mL of HF were added. These vials were inserted into the corresponding steel containers and

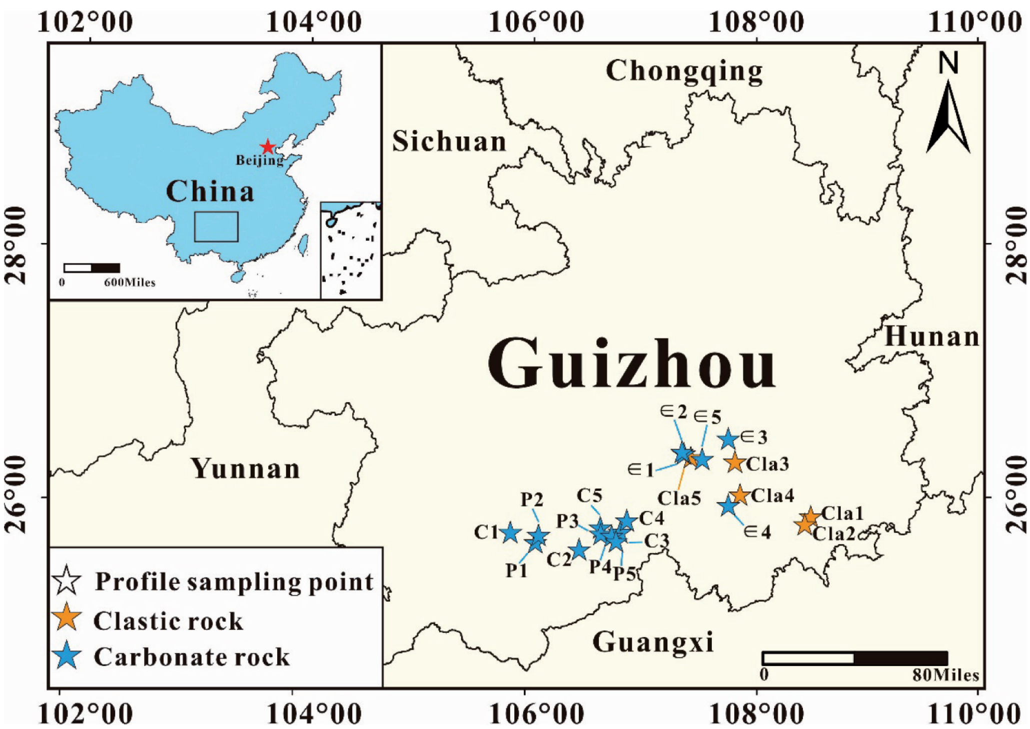

Fig. 1. Location of the study area and distribution of sampling points.

digested for a minimum of 15 hours in a thermostatic incubator. After cooling down, approximately 2mL of 3% dilute nitric acid was added, and the digestion continued for another 5 hours in the thermostatic incubator. Once cooled, the undisturbed solution from the digestion vials was carefully transferred to polyethylene terephthalate (PET) centrifuge tubes and diluted to a final volume of 10mL with ultrapure water. After thorough mixing, the mixture was centrifuged and left undisturbed for 2 to 3 hours before conducting testing. The trace element analysis and testing work was conducted at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The analytical instrument used for this purpose was the Plasma Quant MS Elite Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The relative standard deviation (RSD) of the replicate testing for trace element analysis of all samples was found to be less than 10%, indicating excellent repeatability.

Data Process

Mass Transfer Coefficient (τ)

The mass transfer coefficient is commonly used to evaluate the migration or enrichment degree of trace elements in soil relative to bedrock [44]. It is represented by the following formula:

$$\tau=(X/Zr)s/(X/Zr)r-1$$

In the formula, X represents a certain trace element, while Zr serves as the reference element [45]. The subscripts s and r represent the soil and bedrock samples, respectively. If $\tau > 0$, it indicates the enrichment of the element relative to the bedrock during the weathering process. If $\tau < 0$, it suggests the migration of the element during the weathering of bedrock into the soil. When $\tau = -1$, it indicates complete leaching and loss of the element.

Enrichment Factor (EF)

The enrichment factor is used to characterize the degree of enrichment of trace elements in soil relative to bedrock during the weathering process. It is represented by the following formula:

$$EF=Cxs/Cxr$$

In the formula, Cxs represents the trace element content in soil, and Cxr represents the trace element content in bedrock. If the EF value is greater than 1, it indicates the enrichment of a certain trace element in the soil relative to the bedrock. A higher EF value suggests a higher degree of element enrichment during the weathering process. If the EF value is less than 1, it indicates depletion of a certain trace element in the soil relative to the bedrock.

Mass Fraction (%) of Heavy Metal in Different Mineral Phases

This study is based on the mineral composition and characteristics of carbonate rocks. Carbonate rocks are classified into Acid-Soluble Mineral Phases (ASMP) and Acid-Insoluble Mineral Phases (AIMP). Based on the extraction tests of acid-insoluble components and the trace element analysis of acid-insoluble minerals, the mass fractions of heavy metal elements in both acid-insoluble and acid-soluble mineral phases of carbonate rocks were calculated. The calculation formula is as follows:

$$AIMP\text{-}X\ (\%) = (m\ AIMP\text{-}x * C\ AIMP\text{-}x)\ /Crock\text{-}x * 100\%$$
$$ASMP\text{-}X\ (\%) = 1\text{-}AIMP\text{-}X\ (\%)$$

Table 1. Characteristics of heavy metals content rocks and weathered soils (mg/kg).

Lithology	Samples		Element content (mg/kg)					
			Cr	Ni	Cu	Zn	Cd	Pb
Carbonate rock	Rock N=15	Max	82.9	50.7	9.5	107	0.84	35.2
		Min	3.71	25.9	1.62	2.53	0.02	0.22
		Mean	21.61	36.72	3.21	15.81	0.22	3.8
	Soil N=60	Max	355	113	53.8	480	17.9	244
		Min	19.9	8.65	7.35	23.4	0.106	11.3
		Mean	137	51.2	29.6	169	3.95	57.7
	EF soli/rock		6.34	1.39	9.22	10.69	17.95	15.18
Clastic rock	Rock N=5	Max	189	69.6	40.8	85.45	0.17	80.1
		Min	37.61	41.89	14.85	28.3	0.103	11.22
		Mean	89.57	33.69	27.93	72.7	0.139	31.41
	Soil N=32	Max	104	143	52.2	147	0.26	87.0
		Min	43.3	11.2	16.6	43.2	0.04	15.7
		Mean	66.7	23.4	23.5	70.2	0.128	32.7
	EF soil/rock		0.74	0.69	0.84	0.97	0.92	1.04

In the formula, m AIMP-x represents the mass of acid-insoluble components extracted from carbonate rocks (g), CAIMP-x and Crock-x, respectively, denote the content of a certain heavy metal element in the acid-insoluble components and carbonate rocks (mg/kg).

Results

Characteristics of Heavy Metal Element Content (mg/kg)

This study aimed to investigate the variation characteristics of heavy metal element content during the weathering process of different lithological bedrocks and the differences in elemental geochemical behaviors. The heavy metal element content in weathered profiles of carbonate rocks and clastic rocks in the study area was tested. The content of heavy metal elements in carbonate rocks, clastic rock bedrocks, and their weathered soils in the study area is presented in Table 1. The average content of Cr, Ni, Cu, Zn, Cd, and Pb in carbonate rocks is 21.61, 36.72, 3.21, 15.81, 0.22, and 3.8 mg/kg, respectively. In clastic rock bedrock, the content of Cr, Ni, Cu, Zn, Cd, and Pb is 89.51, 33.69, 27.85, 72.7, 0.139, and 31.41 mg/kg, respectively. Except for Cd, the average heavy metal element content in clastic rock bedrocks is higher than that in carbonate rocks. In weathered soils derived from carbonate rocks, the average content of Cr, Ni, Cu, Zn, Cd, and Pb is 137, 51.2, 29.6, 169, 3.95, and 57.7 mg/kg, respectively. The average content of Cr, Ni, Cu, Zn, Cd, and Pb in weathered soils derived from clastic rocks is 66.7, 23.4, 23.5, 70.2, 0.128, and 32.7 mg/kg, respectively. The heavy metal element content in weathered soils derived from carbonate rocks is higher than that in weathered soils derived from clastic rocks.

The enrichment factor (EF) is commonly used to indicate the degree of enrichment of elements in soil compared to their content in the bedrock. The enrichment fac-

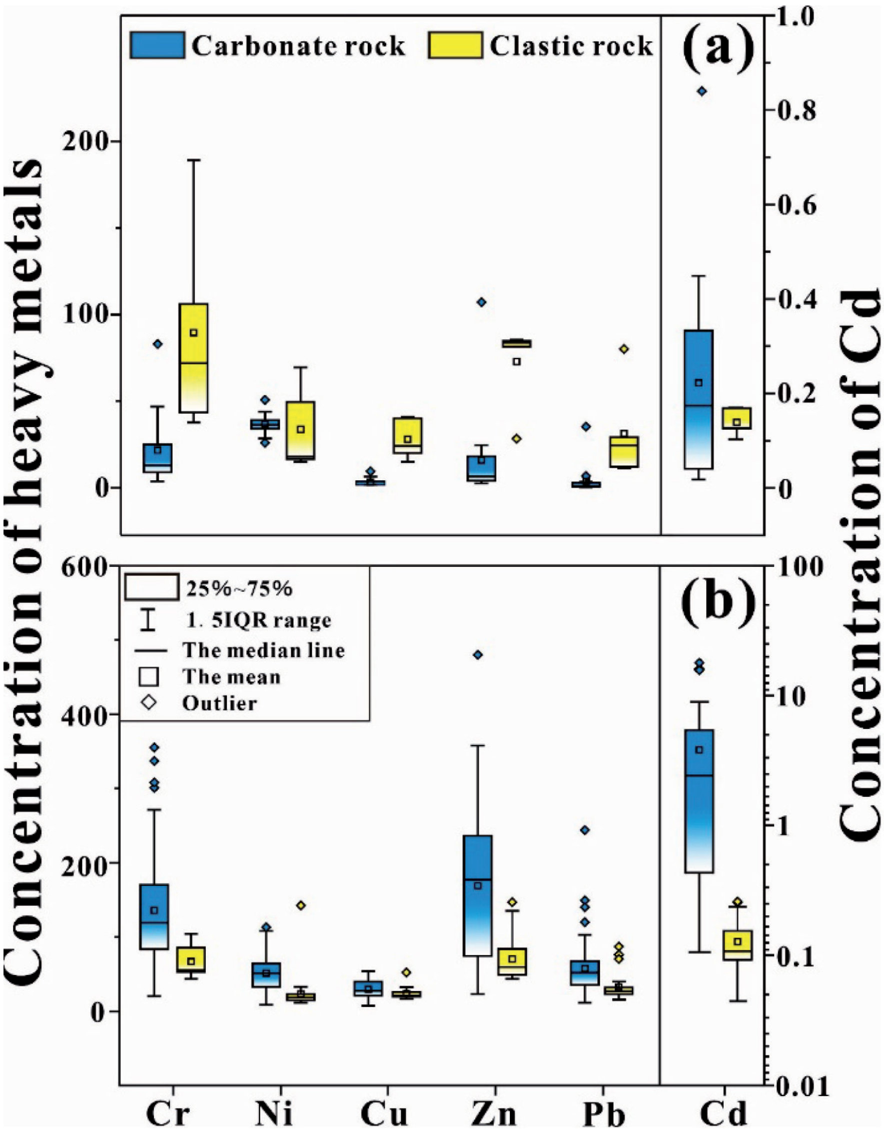

Fig. 2. Characteristics of heavy metal element content (mg/kg). a) bedrock, b) Weathered soil).

tors (EF) of Cr, Ni, Cu, Zn, Cd, and Pb in weathered soils derived from carbonate rocks are 6.34, 1.39, 9.22, 10.69, 17.95, and 15.18, respectively, indicating varying degrees of enrichment of heavy metal elements in the soil compared to the bedrock. In contrast, the EF values for Cr, Ni, Cu, Zn, Cd, and Pb in weathered soils derived from clastic rocks fluctuate around 1, with values of 0.74, 0.69, 0.84, 0.97, 0.92, and 1.04, respectively. This suggests that there is no significant enrichment of heavy metal elements in weathered soils derived from clastic rocks compared to the bedrock (Table 1). Overall, there are significant differences in the geochemical behavior of heavy metal elements during the weathering process of carbonate rocks and clastic rocks. Weathered soils derived from carbonate rocks exhibit a substantial increase in the content of heavy metal elements compared to the parent rock, showing a strong enrichment effect. In contrast, weathered soils derived from clastic rocks mostly inherit the geochemical information of the parent rock, resulting in relatively homogeneous soil heavy metal element content (Fig. 2).

Results of Acid-Insoluble Residue Leaching Tests

The results of microscopic mineral identification and acid-insoluble residue extraction tests for carbonate rocks are presented in Table 2. The rock mineral identification results indicate that, except for the bedrocks from profiles Є1, Є 5, and C5, which are identified as dolomite, the bedrocks from the remaining profiles are limestone. From a geological stratigraphic perspective, the bedrocks of Cambrian profiles are mostly chemical sedimentary rocks, while the Carboniferous and Permian profiles predominantly consist of bioclastic sedimentary rocks. This reflects the variation in the diagenetic background of carbonate rocks during different geological periods within the study area. The acid-insoluble residue extraction test results for carbonate rocks indicate that the content of acid-insoluble residue in Cambrian bedrocks is significantly higher than that in Carboniferous and Permian bedrocks. Specifically, the acid-insoluble residue content in Cambrian bedrock ranges from 1.86% to 38.52%, with an average of 15.21%. In Carboniferous bedrock, the acid-insoluble residue content varies from 0.12% to 3.71%, averaging at 0.95%. For Permian bedrock, the acid-insoluble residue content ranges from 0.12% to 6.66%, with an average of 1.54%. There are variations in the acid-insoluble residue content of carbonate rock bedrock across different geological periods, which is closely associated with material sources during diagenesis and the paleogeographic environment of the lithofacies they were formed in. Studies have shown that the acid-insoluble residue content in carbonate rocks from karst regions in southwest China is generally less than 10% [46]. Overall, the collected bedrocks in this study exhibit a relatively low proportion of acid-insoluble residue, indicating a relatively pure nature of the carbonate rocks.

Table 2. Identification of carbonate rock and results of acid-insoluble residue extraction tests.

Stratum	Samples	Lithology identification	Content of Acid insoluble (%)
Cambrian	Є 1	Doloarenite	3.12
	Є 2	Dolomite limestone	17.16
	Є 3	Powder crystal limestone	1.86
	Є 4	Microcrystalline limestone	15.39
	Є 5	Siliceous clayey dolomite	38.52
	Mean		15.21
Carboniferous	C1	Bioclastic limestone	3.71
	C2	Bioclastic limestone	0.12
	C3	Bioclastic limestone	0.22
	C4	Algae trace limestone	0.12
	C5	Doloarenite	0.60
	Mean		0.95
Permian	P1	Bioclastic limestone	6.66
	P2	Bioclastic limestone	0.15
	P3	Bioclastic limestone	0.48
	P4	Bioclastic limestone	0.30
	P5	Bioclastic limestone	0.12
	Mean		1.54

The abbreviation of the Cambrian is denoted by "Є", the abbreviation of the Carboniferous is denoted by "C" and the abbreviation of the Permian is denoted by "P". For example, Cambrian section 1 is represented as Є 1.

Content Characteristics of Heavy Metal During Weathering of Carbonate Rock (mg/kg)

The characteristic concentrations of heavy metal elements in carbonate bedrock, acid-insoluble substances, and weathered soils of different geological epochs are shown in Table 3. The order of Cu, Zn, and Pb concentrations in carbonate bedrock from different geological epochs is as follows: Cambrian > Carboniferous > Permian, while the order of Cr and Ni concentrations is Cambrian > Permian > Carboniferous. However, the Cd concentration exhibits the reverse order, showing Permian > Carboniferous > Cambrian (Fig. 3a). The order of Cr, Ni, Cu, Zn, and Cd concentrations in acid-insoluble substances from different geological epochs is Carboniferous > Permian > Cambrian, whereas the order for Pb concentration is Carboniferous > Cambrian > Permian (Fig. 3b). Regarding weathered soils from different geological epochs of carbonate bedrock, the order of Cr, Ni, Cu, and Cd concentrations is Permian > Carboniferous > Cambrian, while the order for Zn concentration is Permian > Cambrian > Carboniferous. The order for Pb concentration is Cambrian > Permian > Carboniferous (Fig. 3c). Overall, the concentration of heavy metal elements in the Cambrian carbonate bedrock is higher than that in the Carboniferous and Permian epochs. On the other hand, the concentrations of heavy metal elements in acid-insoluble substances and weathered soils show that the Carboniferous and Permian epochs have higher levels compared to the Cambrian epoch. The distribution patterns of heavy metal elements in acid-insoluble substances and soils exhibit closer similarities.

The enrichment factors of heavy metal elements in weathered soils of carbonate bedrock from different geological epochs are shown in Table 4. The enrichment factors for Cr, Ni, Cu, Zn, Cd, and Pb in the Cambrian epoch are 2.37, 1.00, 5.71, 4.88, 6.63, and 7.58, respectively. For the Carboniferous epoch, the enrichment factors for Cr, Ni, Cu, Zn, Cd, and Pb are 14.16, 1.46, 10.30, 17.58, 17.33, and 93.52, respectively. In the Permian epoch, the enrichment factors for Cr, Ni, Cu, Zn, Cd, and Pb are 12.28, 1.76, 16.69, 41.26, 20.97, and 53.57, respectively. It can be observed that the degree of enrichment of heavy metal elements in weathered soils of Carboniferous and Permian carbonate bedrock is significantly higher than that of the Cambrian epoch.

Discussion

The Control Effect of Weathering Patterns

Soil is the weathering product of parent rock, and they both have a natural material inheritance [47]. From

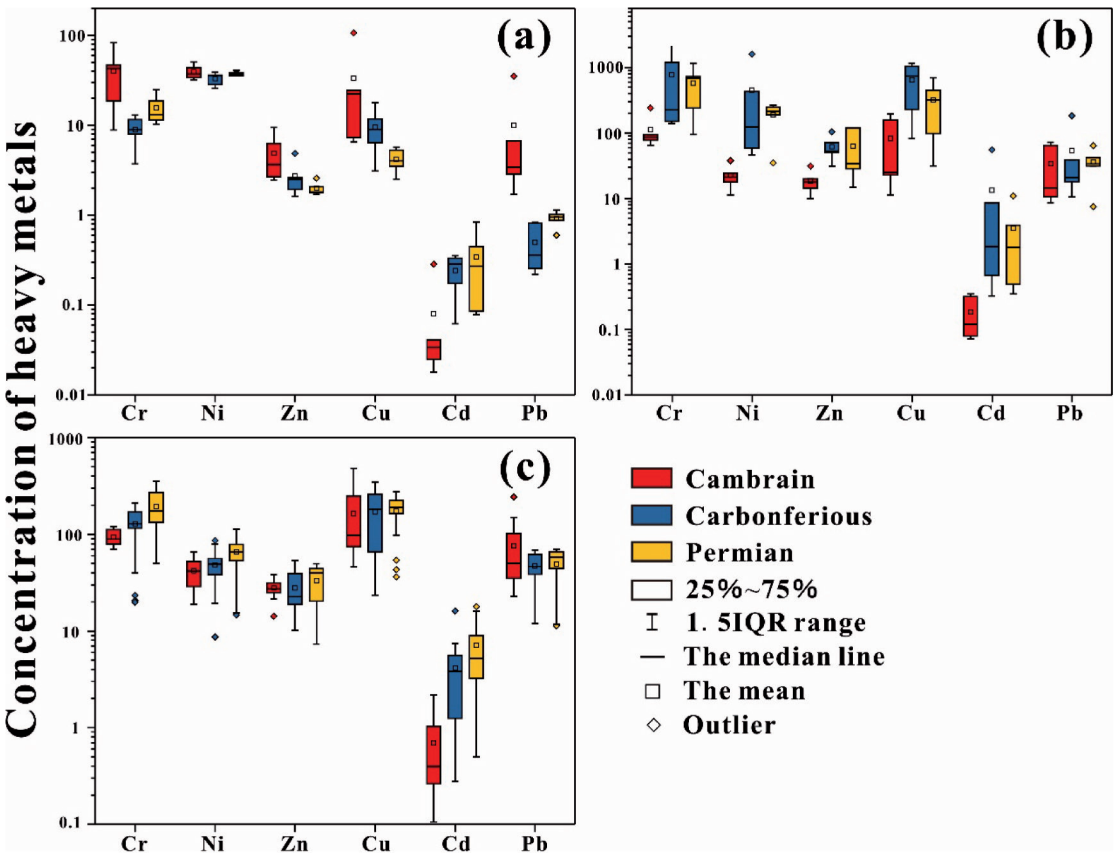

Fig. 3. Characteristics of heavy metal content in weathering process of carbonate rock (mg/kg). a) Carbonate, b) Acid-insoluble Substances, C) Weathered Soil.

Table 3. Characteristics of heavy metals content during weathering of carbonate rock(mg/kg).

Stratum	Samples		Cr	Ni	Cu	Zn	Cd	Pb
Cambrian	Rock N=5	Max	82.9	50.7	9.50	107.00	0.29	35.20
		Min	8.88	32.1	2.47	6.55	0.02	1.71
		Mean	40.1	39.6	4.92	33.56	0.08	9.99
	Acid non-soluble substance N=5	Max	241	37.9	31.2	195	0.349	72
		Min	65.1	11.3	9.99	11.3	0.072	8.62
		Mean	113	22.54	18.698	82.32	0.188	34.004
	Soil N=21	Max	120	64.80	38.30	480.00	1.37	244.00
		Min	70.2	18.80	14.20	46.00	0.11	22.90
		Mean	94.9	39.60	28.11	163.92	0.53	75.72
	EF soli/rock		2.37	1.00	5.71	4.88	6.63	7.58
Carboniferous	Rock N=5	Max	13.0	39.00	4.88	18.00	0.36	0.83
		Min	3.71	25.90	1.62	3.11	0.06	0.22
		Mean	9.04	33.08	2.71	9.66	0.24	0.50
	Acid insoluble substance N=5	Max	2138	1605	104.29	1151	55.6	183.59
		Min	139	46.2	31.25	82.5	0.33	10.55
		Mean	768	452.7	60.02	649	13.41	54.42
	Soil N=21	Max	212	86.50	53.80	346.00	16.10	68.90
		Min	19.9	8.65	10.20	23.40	0.28	11.90
		Mean	128	48.43	27.91	169.85	4.16	46.76
	EF soli/rock		14.16	1.46	10.30	17.58	17.33	93.52
Permian	Rock N=5	Max	24.9	41.00	2.58	5.68	0.84	1.14
		Min	10.3	35.50	1.71	2.53	0.08	0.60
		Mean	15.8	37.50	1.99	4.21	0.34	0.92
	Acid insoluble substance N=5	Max	1151	266	120	698	10.96	42.01
		Min	95.5	35.1	14.75	31.5	0.35	7.55
		Mean	579	191	63.49	320	3.93	28.71
	Soil N=18	Max	355	113	49.6	278	17.90	70.10
		Min	50.0	14.65	7.35	36.35	0.50	11.30
		Mean	194	65.93	33.22	173.69	7.13	49.28
	EF soli/rock		12.28	1.76	16.69	41.26	20.97	53.57

a material structure perspective, the differences in lithology are essentially differences in mineral composition. The variations in mineral composition among different lithologies can undoubtedly affect the geochemical behavior of elements during the weathering-to-soil process [48]. Clastic rocks are primarily composed of silicate minerals (feldspar, quartz, and clay minerals) and tend to exhibit strong resistance to weathering, presenting an isotropic weathering pattern. Carbonate rocks are mainly composed of carbonate minerals (calcite, dolomite), and during the weathering-to-soil process, the rock-forming elements such as Ca and Mg are extensively leached by weathering fluids, resulting in significant loss of their mass and volume, thus reflecting a non-isotropic weathering pattern.

This study calculated the correlation between the enrichment factors and mass transfer coefficients of heavy metal elements in weathered soils derived from clastic rocks and carbonate rocks (Fig. 4). The results indicate a significant and strong positive correlation between the enrichment factors and mass transfer coefficients of Cr, Ni, Cu, Zn, Cd, and Pb in weathered soils derived from clastic rocks, with R-squared values of 0.9335, 0.9977, 0.9139, 0.8337, 0.5642, and 0.9826, respectively. This suggests that under the constraint of isotropic weathering patterns, the accumulation of heavy metal elements in weathered soils derived from clastic rocks is primarily controlled by the extent of element migration. In other words, without the addition of exogenous heavy metal elements, the soil tends to inherit the heavy metal element content from its parent rock. In contrast, for weathered soils derived from carbonate rocks, there is no linear relationship between the enrichment factors and mass transfer coefficients of Cr, Ni, Cu, Zn, Cd, and Pb. Moreover, significant enrichment occurs even when a substantial portion of the heavy metal elements have

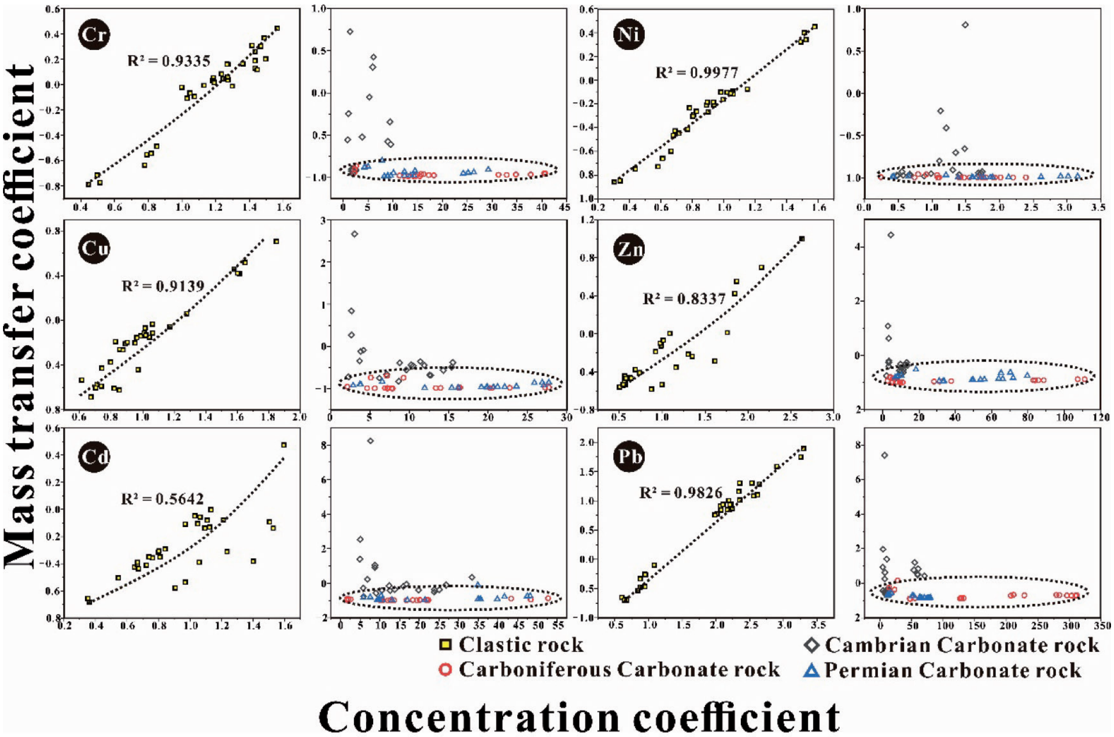

Fig. 4. Correlation between Enrichment Factors and Mass Transfer Coefficients.

been leached (Fig. 4). The reason behind this phenomenon is closely related to the distinct weathering pattern exhibited by carbonate rocks.

The weathering-to-soil process of carbonate rocks can generally be divided into two stages. During the early stage of weathering, carbonates dissolve, resulting in a significant loss of Ca and Mg ions. In the later stage, weathering mainly involves the deep weathering of silicate minerals [42, 49]. Intense leaching occurs during the weathering-to-soil process of carbonate rocks, leading to the profound natural evolution of elements and substances. In this study, due to the differences in lithology, carbonate rocks and clastic rocks display distinct geochemical behaviors of heavy metal elements during weathering-to-soil processes. The enrichment factors of heavy metal elements in weathered soils derived from clastic rocks fluctuate around a baseline value of 1. In contrast, the enrichment factors of heavy metal elements in weathered soils derived from carbonate rocks can reach values above ten, with Pb being enriched 78 times compared to the parent rock. This means that even in carbonate rocks with relatively depleted heavy metal content [50], significant enrichment of various trace elements, including heavy metals, occurs during the weathering-to-soil process. Therefore, the accumulation of heavy metal elements during the weathering-to-soil process of carbonate rocks can be understood as the result of the absolute mass loss of elements and the relative enrichment of their concentrations. The unique non-isotropic weathering pattern of carbonate rocks plays an important role in this phenomenon.

The Influence of Acid-Insoluble Residues in Carbonate Rocks

The previous discussion demonstrated that the unique weathering pattern of carbonate rocks leads to significant enrichment of heavy metal element content. However, despite this finding, there are considerable differences in the geochemical behavior of heavy metal elements during the weathering-to-soil process of carbonate rocks from different geological epochs. The leaching and enrichment levels of heavy metal elements in weathered soils derived from Carboniferous and Permian carbonate rocks are notably higher than those from the Cambrian epoch (Fig. 4). This study attempts to clarify these differences from the perspective of acid-insoluble residues in carbonate rocks.

In the natural weathering process of rocks, the fate of elements is often closely related to the minerals in which they are present [51]. Therefore, to understand the geochemical behavior of heavy metal elements during the weathering of carbonate rocks, it is important to first clarify the occurrence characteristics of these elements in different mineral phases. Carbonate rocks are primarily composed of easily soluble carbonate minerals and insoluble silicate minerals. The former is the main rock-forming mineral of carbonate rocks, which is extensively leached by weathering fluids during the weathering-to-soil process. On the other hand, the latter remains a residue during the weathering-to-soil process and represents the major soil-forming material of carbonate rocks. Based on the mineral composition characteristics of carbonate rocks, this study divides carbonate

Table 4. Enrichment factor of heavy metal elements in the weathering process of carbonate rocks.

Stratum		Cr	Ni	Cu	Zn	Cd	Pb
Cambrian	EF1	2.83	0.57	3.80	2.45	2.33	3.40
	EF2	0.83	1.86	1.49	1.99	3.69	2.23
Carboniferous	EF1	85.13	13.68	22.87	67.20	55.31	109.40
	EF2	0.17	0.11	0.45	0.26	0.31	0.86
Permian	EF1	36.79	5.09	31.84	76.09	10.15	38.97
	EF2	0.33	0.35	0.52	0.54	2.04	1.38

EF1 represents the ratio of a certain metal element content in acid-insoluble components to that in rocks, while EF2 represents the ratio of a certain metal element content in soil to that in acid-insoluble. Units have no dimension.

rocks into two end-members: The Acid-Soluble Mineral Phase (ASMP) and the Acid-Insoluble Mineral Phase (AIMP). The acid-soluble mineral phase represents carbonate minerals, while the acid-insoluble mineral phase partially represents the characteristics of residual dissolution products. Therefore, to unravel the geochemical behavior of heavy metal elements during the weathering process of carbonate rocks, understanding the occurrence and behavior of these elements in the acid-soluble and acid-insoluble mineral phases is crucial. Based on the results of acid-insoluble residue extraction tests (Table 3) and heavy metal element content analysis in acid-insoluble residues (Table 4), this study calculated the mass fraction of heavy metal elements in different mineral phases of carbonate rocks. The calculations indicate that heavy metal elements are distributed among various mineral phases of carbonate rocks, but overall, they tend to occur more in the acid-soluble mineral phase (Fig. 5). Furthermore, there exists a distribution pattern where higher acid-insoluble residue content is associated with a greater tendency for heavy metal elements to occur in the acid-insoluble mineral phase. For instance, in Profile Є5, where the acid-insoluble residue content is 38.52%, heavy metal elements are predominantly present in the acid-insoluble mineral phase. Conversely, in Profile Є3, with an acid-insoluble residue content of 1.86%, heavy metal elements are mostly found in the acid-soluble mineral phase. It can be said that the acid-insoluble residue content controls the mass distribution of heavy metal elements in different mineral phases of carbonate rocks, and this distribution characteristic determines the fate of heavy metal elements during the weathering-to-soil process to some extent. The lower acid-insoluble residue content in Carboniferous and Permian carbonate rocks results in less residual soil-forming material during their weathering-to-soil process. As a consequence, the degree of weathering experienced by these rocks is more intense, which explains why the leaching of heavy metal elements in the weathered soils derived from Carboniferous and Permian carbonate rocks is higher compared to the Cambrian period.

Previous studies have provided mineralogical and geochemical evidence to demonstrate that the overlying soil in karst areas is the in-situ weathering residue

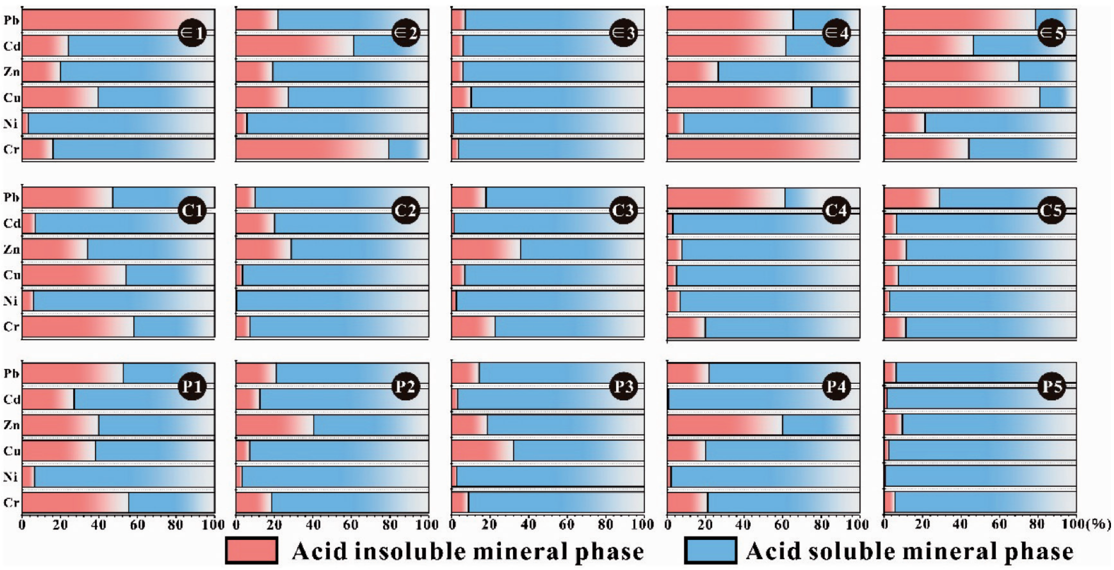

Fig. 5. Mass percentage of heavy metals in different mineral phases (%).

of acid-insoluble minerals from the underlying bedrock [42,49]. In this study, we introduced acid-insoluble minerals as a 'bridge' connecting the elemental geochemical information between carbonate bedrock and soil. The process of carbonate rock weathering into the soil was divided into two stages: 1. Bedrock-dissolved residue (acid-insoluble minerals) and 2. Dissolved residue-soil. Enrichment factors for heavy metal elements were calculated separately for these two stages (Table 4) in our research. The calculation results indicated that heavy metal elements generally exhibited enrichment characteristics during the first stage, with coal and Permian strata showing significantly higher enrichment factors compared to the Cambrian strata. This reflects the concentration enrichment of heavy metal elements due to the extensive leaching of carbonate minerals during the weathering stage, from bedrock to dissolved residue. However, the enrichment factors of heavy metal elements noticeably decreased in the second stage, even displaying depletion characteristics. This suggests that during the evolution of dissolved residue into soil under the influence of weathering and leaching processes, heavy metal elements partially migrated out of the system. The content of heavy metal elements during the process of carbonate rock weathering into the soil demonstrated an initial significant increase followed by a slight decrease, implying that acid-insoluble minerals greatly influence the distribution characteristics of heavy metal elements in soil. To verify this hypothesis, this study conducted a correlation analysis between the content of heavy metal elements in acid-insoluble minerals from carbonate rocks and weathered soil. The results indicated variations in the correlation between acid-insoluble minerals from different geological eras and the content of heavy metal elements in weathered soil. Specifically, the correlation was relatively strong for the Cambrian and Permian strata, while it was weaker for the Carboniferous strata (Fig. 6). The weak correlation between acid-insoluble minerals from the Carboniferous strata and the content of heavy metal elements in weathered soil can be attributed to their lower acid-insoluble mineral content (ranging from 0.12% to 3.71%, with a mean value of 0.95%). The poor correlation between acid-insoluble minerals and the Ni content in weathered soil for the Cambrian, Carboniferous, and Permian strata also supports this notion, as Ni is predominantly associated with acid-soluble mineral phases, which are prone to intense leaching during the process of weathering into the soil (Fig. 5). Additionally, the weak correlation observed between acid-insoluble minerals from the Carboniferous strata and the content of Cu, Zn, and Pb in weathered soil suggests a similar control factor affecting these chemically akin chalcophile elements [52] during the process of weathering into the soil.

The correlation between the content of heavy metal elements in acid-insoluble minerals from carbonate rocks and weathered soil does not exhibit a simple linear relationship across different geological eras. This indicates that the geochemical behavior of heavy metal elements during the process of carbonate rock weathering into the soil is influenced by multiple factors, making it a complex natural evolutionary process. However, overall, the concentration of heavy metal elements in acid-insoluble minerals from carbonate rocks partially controls the characteristics of heavy metal element content in weathered soil. The Carboniferous and Permian strata exhibit significantly higher concentrations of heavy metal elements in their acid-insoluble minerals compared to the Cambrian strata. Consequently, the corresponding weathered soil inherits this distribution characteristic of the heavy metal element content. This constitutes an important reason for

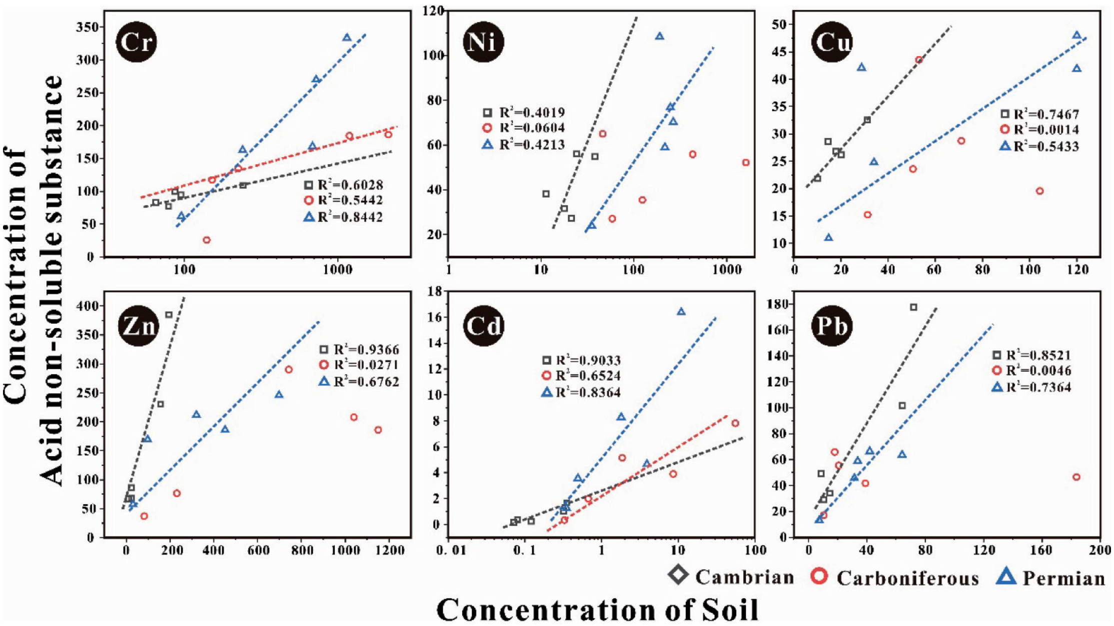

Fig. 6. Correlation between the content of heavy metal elements (mg/kg).

the variations in the enrichment levels of heavy metal elements in weathered soil derived from carbonate rocks of different geological periods.

Ecological Risk Assessment and Consideration

Soil background values of elements are commonly used as important reference values to assess whether the content of elements in the soil exceeds the standard limits. In this study, the unique weathering patterns of carbonate rocks resulted in a significant enrichment effect of heavy metal elements. This is a major contributing factor to the excessive content of heavy metal elements in weathered soil derived from carbonate rocks. The study utilized soil element background values in Guizhou Province as standards for defining exceeding content [23]. The Carboniferous and Permian strata in the study area exhibited seriously elevated levels of heavy metal elements in weathered soil. The exceeding rates were 77% for Cr, 79% for Ni, 46% for Cu, 69% for Zn, 85% for Cd, and 79% for Pb, respectively. Particularly, the Cd content in the overlying soil of the C2 profile in the Carboniferous series (with an average of 7.82 mg/kg) and the P2 profile in the Permian series (with an average of 16.38 mg/kg) showed severely elevated levels. Such high concentrations of heavy metal elements in natural areas are alarming. Although previous studies on ecological risk in karst regions have indicated that the alkaline soil environment restricts the biogeochemical cycling of heavy metal elements and does not pose significant ecological risks [31, 40], it should be noted that sudden changes in external environmental conditions such as temperature, pH, Eh, etc. can promote the transformation of heavy metal element forms [53, 54]. Taking Guizhou Province as an example, in the past 30 years (1980-2010), the cultivated land in the province has shown an overall trend of acidification, primarily caused by global climate warming and the widespread application of agricultural fertilizers [55].

Therefore, it is necessary for us to re-examine the ecological and environmental risks posed by heavy metal elements in karst regions. It is recommended that local governments and relevant departments pay close attention to the dynamic anomalies of heavy metal elements in special areas. This can help reduce the uncontrolled diffusion of heavy metal elements into the surrounding environment. While strict control measures for industrial and agricultural pollution are implemented, physical, chemical, and biological remediation methods should be adopted to reduce the content of heavy metal elements in the soil. Additionally, since heavy metal elements present in the acid-soluble mineral phases of carbonate rocks can be released and migrated during the initial stages of weathering, it may result in natural regional diffuse sources. Although the Cd content in the acid-soluble mineral phases of carbonate rocks is significantly lower compared to that in the acid-insoluble mineral phases, the alkaline geological environment in karst areas can cause adsorption and retention effects on trace metal elements like Cd. Furthermore, this enrichment effect may be intensified in watercourse sediments. Therefore, this study suggests that the presence of heavy metal elements in surface runoff and karst groundwater in karst regions should also be given attention to avoid the transformation of geological 'high background' areas into geological 'high-risk' areas.

Conclusions

This study investigates the enrichment mechanisms of heavy metal elements in weathered carbonate rock soils under natural background conditions. The findings provide the following insights:

(1) The geochemical behaviors of heavy metal elements during the weathering process of carbonate rock and clastic rock in the study area exhibit distinct differences. The enrichment and accumulation of heavy metal elements in weathered carbonate rock soils result from an absolute loss of element mass and a relative enrichment of element content.

(2) The content of acid-insoluble components in carbonate rocks controls the mass distribution of heavy metal elements in different mineral phases and influences the geochemical behavior of heavy metal elements during the weathering process. This is an important factor contributing to the high migration and enrichment of heavy metal elements in Carboniferous and Permian weathered carbonate rock soils compared to Cambrian soils.

(3) The excessive levels of heavy metal elements in weathered carbonate rock soils are more serious in the Carboniferous and Permian formations. Considering the unique weathering patterns of carbonate rocks, in addition to strengthening the monitoring of excessive levels of heavy metal elements in overlying soils in special formations, attention should also be given to the heavy metal element content in surface runoff and groundwater.

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Conflict of Interest

The authors declare no conflict of interest.

References

1. WANG Z., LUO P.P., ZHA X.B., XU C.Y., KANG S.X., ZHOU M.M., NOVER D., WANG Y.H. Overview assessment of risk evaluation and treatment technologies for heavy metal pollution of water and soil. Journal of Cleaner Production, **379**, 134043, **2022**.
2. QIN G.W., NIU Z.D., YU J.D., LI Z.H., MA J.Y., XIANG P. Soil heavy metal pollution and food safety in China: Effects, sources and removing technology. Chemosphere, **267**, 129205, **2021**.
3. LIU L., LI W., SONG W., GUO M. Remediation techniques for heavy metal-contaminated soils: Principles and applicability. Science of the Total Environment, **633**, 206, **2018**.
4. WU Y.F., LI X., YU L., WANG T.Q., WANG J.N., LIU T.T. Review of soil heavy metal pollution in China: Spatial distribution, primary sources, and remediation alternatives. Resources Conservation and Recycling, **181**, 106261, **2022**.
5. CAI Y., HAN Z., LU H., ZHAO R., WEN M., LIU H., ZHANG B. Spatial-temporal variation, source apportionment and risk assessment of lead in surface river sediments over ~20 years of rapid industrialisation in the Pearl River Basin, China. Journal of Hazardous Materials, **464**, 132981, **2024**.
6. RAJENDRAN S., PRIYA T.A.K., KHOO K.S., HOANG T.K.A., NG H.S., MUNAWAROH H.S.H., KARAMAN C., OROOJI Y., SHOW P.L. A critical review on various remediation approaches for heavy metal contaminants removal from contaminated soils. Chemosphere, **287**, 132369, **2022**.
7. LI Q., WANG Y.H., LI Y.C., LI L.F., TANG M.D., HU W.F., CHEN L., AI S.Y. Speciation of heavy metals in soils and their immobilization at micro-scale interfaces among diverse soil components. Science of the Total Environment, **825**, 153862, **2022**.
8. SHI J.D., ZHAO D., REN F.T., HUANG L. Spatiotemporal variation of soil heavy metals in China: The pollution status and risk assessment. Science of the Total Environment, **871**, 161768, **2023**.
9. GAO J., GONG J., YANG J., WANG Z., FU Y., TANG S., MA S. Spatial distribution and ecological risk assessment of soil heavy metals in a typical volcanic area: Influence of parent materials. Heliyon, **9** (1), e12993, **2023**.
10. HU B., SHAO S., NI H., FU Z., HUANG M., CHEN Q., SHI Z. Assessment of potentially toxic element pollution in soils and related health risks in 271 cities across China. Environmental Pollution, **270**, 116196, **2021**.
11. PENG J.Y., ZHANG S., HAN Y.Y., BATE B., KE H., CHEN Y.M. Soil heavy metal pollution of industrial legacies in China and health risk assessment. Science of the Total Environment, **816**, 151632, **2022**.
12. REN S., SONG C., YE S., CHENG C., GAO P. The spatiotemporal variation in heavy metals in China's farmland soil over the past 20 years: A meta-analysis. Science of the Total Environment, **806**, 150322, **2022**.
13. UL HAQUE F., FARIDULLAH, FAWAD M., IRSHAD M., ABBASI U., MEHMOOD Q., HAFEEZ F., IQBAL A. Characterization of Heavy Metals in Soil as Affected by Different Land Uses in Northern Pakistan. Polish Journal of Environmental Studies, **32** (1), 559, **2023**.
14. QUEZADA-HINOJOSA R.P., FOLLMI K.B., VERRECCHIA E., ADATTE T., MATERA V. Speciation and multivariable analyses of geogenic cadmium in soils at Le Gurnigel, Swiss Jura Mountains. Catena, **125**, 10, **2015**.
15. LIU Y.Z., XIAO T.F., PERKINS R.B., ZHU J.M., ZHU Z.J., XIONG Y., NING Z.P. Geogenic cadmium pollution and potential health risks, with emphasis on black shale. Journal of Geochemical Exploration, **176**, 42, **2017**.
16. LIU Y.Z., XIAO T.F., ZHU Z.J., MA L., LI H., NING Z.P. Geogenic pollution, fractionation and potential risks of Cd and Zn in soils form a mountainous region underlain by black shale. Science of The Total Environment, **760** (1), 143426, **2020.**
17. BOCARDI J.M.B., PLETSCH A.L., MELO V.F., QUINAIA S.P. Quality reference values for heavy metals in soils developed from basic rocks under tropical conditions. Journal of Geochemical Exploration, **217**, 106591, **2020**.
18. STRBAC S., RANDELOVIC D., GAJICA G., HUKIC E., STOJADINOVIC S., VESELINOVIC G., ORLIC J., TOGNETTI R., KAS M. Spatial distribution and source identification of heavy metals in European mountain beech forests soils. Chemosphere, **309**, 136662, **2022**.
19. WANG K.L., ZHANG C.H., CHEN H.S., YUE Y.M., ZHANG W., ZHANG M.Y., QI X.K., FU Z.Y. Karst landscapes of China: patterns, ecosystem processes and services. Landscape Ecology, **34** (12), 2743, **2019**.
20. LIU J., LI X.Y., ZHANG P.Y., ZHU Q.L., LU W.H., YANG Y.Q., LI Y., ZHOU J.W., WU L.H., ZHANG N.M., CHRISTIE P. Contamination levels of and potential risks from metal(loid)s in soil-crop systems in high geological background areas. Science of the Total Environment, **881**, 163405, **2023**.
21. JIA Z., WANG J., ZHOU X., ZHOU Y., LI Y., LI B., ZHOU S. Identification of the sources and influencing factors of potentially toxic elements accumulation in the soil from a typical karst region in Guangxi, Southwest China. Environmental Pollution, **256**, 113505, **2020**.
22. XIAO J., CHEN W., WANG L., ZHANG X., WEN Y., BOSTICK B.C., WEN Y., HE X., ZHANG L., ZHUO X., HUANG K., WANG N., JI J., LIU Y. New strategy for exploring the accumulation of heavy metals in soils derived from different parent materials in the karst region of southwestern China. Geoderma, **417**, 115806, **2022**.
23. CEMS (China Environmental Monitoring Station). Background values of soil elements in China. China Environmental Science Press: Beijing China, **1990** [in Chinese].
24. HE S.L., LONG C.L., LIU Y.Z., HUANG D.G., Yuan Y.S., YI S.W. Geochemistry and Environment of the Cadmium in the Soil and Sediments at the Surface of Guizhou Province. Guizhou Geology, **21** (4), 245, **2004** [in Chinese].
25. WEI X., BAI X., WEN X., LIU L., XIONG J., YANG C. A large and overlooked Cd source in karst areas: The migration and origin of Cd during soil formation and erosion. Science of the Total Environment, **895**, 165126, **2023**.
26. TAO H., LIAO X., LI Y., XU C., ZHU G., CASSIDY D.P. Quantifying in fluences of interacting anthropogenic-natural factors on trace element accumulation and pollution risk in karst soil. Science of the Total Environment, **721**, 137770, **2020**.
27. YANG Q., YANG Z., FILIPPELLI G.M., JI J., JI W., LIU X., WANG L., YU T., WU T., ZHUO X., ZHANG Q. Distribution and secondary enrichment of heavy metal elements in karstic soils with high geochemical background in Guangxi, China. Chemical Geology, **567**, 120081, **2021**.
28. LI W.J., ZHU T.B., YANG H., ZHANG C.L., ZOU X. Distribution Characteristics and Risk Assessment of Heavy Metals in Soils of the Typical Karst and Non-Karst Areas. Land, **11**, 1346, **2022**.
29. WU Y., TIAN X., WANG R., ZHANG M., WANG S. Effects of vegetation restoration on distribution characteristics of heavy metals in soil in Karst plateau area of Guizhou. Peerj, **11**, e15044, **2023**.
30. JI W., LU Y., YANG M., WANG J., ZHANG X., ZHAO C., XIA B., WU Y., YING R. Geochemical Characteristics of

Typical Karst Soil Profiles in Anhui Province, Southeastern China. Agronomy-Basel, **13** (4), 1067, **2023**.

31. WEN Y., LI W., YANG Z., ZHUO X., GUAN D.-X., SONG Y., GUO C., JI J. Evaluation of various approaches to predict cadmium bioavailability to rice grown in soils with high geochemical background in the karst region, Southwestern China. Environmental Pollution, **258**, 113645, **2020**.
32. XIA X., JI J., YANG Z., HAN H., HUANG C., LI Y., ZHANG W. Cadmium risk in the soil-plant system caused by weathering of carbonate bedrock. Chemosphere, **254**, 126799, **2020**.
33. JIANG Z., YANG S., LUO S. Source analysis and health risk assessment of heavy metals in agricultural land of multi-mineral mining and smelting area in the Karst region - a case study of Jichangpo Town, Southwest China. Heliyon, **9** (7), e17246, **2023**.
34. WEN Y., LI W., YANG Z., ZHANG Q., JI J. Enrichment and source identification of Cd and other heavy metals in soils with high geochemical background in the karst region, Southwestern China. Chemosphere, **245**, 125620, **2020**.
35. ZHAO Y., DENG Q., LIN Q., ZENG C., ZHONG C. Cadmium source identification in soils and high-risk regions predicted by geographical detector method. Environmental Pollution, **263**, 114338, **2020**.
36. QIN Y., ZHANG F., XUE S., MA T., YU L. Heavy Metal Pollution and Source Contributions in Agricultural Soils Developed from Karst Landform in the Southwestern Region of China. Toxics, **10** (10), 568, **2022**.
37. WANG J., BAI X., LIU F., ZHANG J., CHEN F., LU Q. Enrichments of Cadmium and Arsenic and Their Effects on the Karst Forest Area. International Journal of Environmental Research and Public Health, **16** (23), 4665, **2019**.
38. WANG Q.Y., WEN X.F., WEI X., LIU H.Y. Heavy Metal Migration and Enrichment Mechanism and the Environmental Risks during the Weathering and Soil Formation of Carbonate Rocks. Earth and Environment, **50** (1), 119, **2021** [in Chinese].
39. FENG Z.Z., LIU W., ZHANG L., LI P.S., MA Q. Enrichment and supernormal enrichment phenomenon of Cd in soils developed on Cd-poor carbonate rocks. Geological Bulletin of China, **41** (4), 533, **2022** [in Chinese].
40. XIA X., JI J., ZHANG C., YANG Z., SHI H. Carbonate bedrock control of soil Cd background in Southwestern China: Its extent and influencing factors based on spatial analysis. Chemosphere, **290**, 133390, **2022**.
41. SUN C.X., WANG S.J., ZHOU D.Q., LIU X.M., JI H.B. Insoluble residues of carbonate rocks as source material for red weathering crusts in karst regions of Guizhou province, China. Acta Mineralogica Sinica, (03), 235, **2002** [In Chinese].
42. JI H.B., WANG S.J., OUYANG Z.Y., ZHANG S., SUN C.X., LIU X.M., ZHOU D.Q. Geochemistry of red residua underlying dolomites in karst terrains of Yunnan-Guizhou Plateau I. The formation of the Pingba profile. Chemical Geology, **203**, 1, **2004.**
43. Regional geology of Guizhou Province. Geological Survey Institute of Guizhou Province: Guiyang, China, **2017** [In Chinese].
44. NESBITT H.W. Mobility and fractionation of rare earth elements during weathering of a granodiorite. Nature, **279**, 206, **1979**.
45. FENG Z.G., LIU X.Z., HAN S.L., MA Q. Study on geochemical behavior of high field strength elements during weathering of carbonate rocks: Evidence from leaching experiment on carbonate rock. Carsologica Sinica, **37** (3), 316, **2018** [in Chinese].
46. SUN C.X., WANG S.J., ZHOU D.Q., LI R.L., LI Y.L. Differential weathering and pedogenetic characteristics of carbonate rocksand their effect on the development of rock desertification in karst regions. Acta Mineralogica Sinica, (04), 308, **2002** [In Chinese].
47. VELBEL M.A., DOMATELLE A.R., FORMOLO M.J. Reactant-product textures, volume relations, and implications for major-element mobility during natural weathering of hornblende, Tallulah Falls Formation, Georgia Blue Ridge, U.S.A. American Journal of Science, **309** (8), 661, **2009**.
48. LARA M.C., BUSS H.L., PETT-RIDGE J.C. The effects of lithology on trace element and REE behavior during tropical weathering. Chemical Geology, **500**, 88, **2018**.
49. WANG S.J., JI H.B., OUYANG Z.Y., ZHOU D.Q., ZHEN L.P., LI T.Y. Preliminary study on weathering and pedogenesis of carbonate rock. Chinese Science: Direct: D, **42** (6), 573, **1999**.
50. KUBIER A., WILKIN R.T., PICHLER T. Cadmium in soils and groundwater: A review. Applied Geochemistry, **108**, 104388, **2019**.
51. PAVONI E., CROSERA M., PETRANICH E., FAGANELI J., KLUN K., OLIVERI P., COVELLI S., ADAMI G. Distribution, Mobility and Fate of Trace Elements in an Estuarine System Under Anthropogenic Pressure: the Case of the Karstic Timavo River (Northern Adriatic Sea, Italy). Estuaries and Coasts, **44** (7), 1831, **2021**.
52. WU T., HUANG Z.L., HE Y.F., YANG M., FAN H.F., WEI C., YE L., HU Y.S., XIANG Z.Z., LAI C.K. Metal source and ore-forming process of the Maoping carbonate-hosted Pb-Zn deposit in Yunnan, SW China: Evidence from deposit geology and sphalerite Pb-Zn-Cd isotopes. Ore Geology Reviews, **135**, 104214, **2021**.
53. LUO F., BA J.J. Migration of heavy metals in karst underground river system. China Mining Magazine, **28** (1), 349, **2019** [In Chinese].
54. ZHANG W., XIN C., YU S. A Review of Heavy Metal Migration and Its Influencing Factors in Karst Groundwater, Northern and Southern China. Water, **15** (20), 3690, **2023**.
55. HUANG Z.Y., IU H.Y., RAN X.Z., WANG X.W., PU L.M. Spatial and Temporal Distribution of Soil pH in Guizhou Province. Journal of Mountain Agriculture and Biology, **39** (4), 21, **2020** [In Chinese].