

Enrichment of heavy metal elements and their adsorption on iron oxides during carbonate rock weathering process

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Abstract

Analysis of trace elements in the Lower Palaeozoic carbonate rock strata of the Beijing area shows that the Cr, Zn, Cd and Pb contents increase from primary carbonate rocks to weathered carbonate rocks and from primary carbonate rocks to the soil coexisting with carbonate rock. Distributions of Cr, Zn, Cd and Pb have the same trends as that of Fe₂O₃. Iron oxides play different roles at different stages of weathering of carbonate rock. The adsorption of Cr, Zn, Cd and Pb on Fe₂O₃ is greater than on FeO in soil. However, FeO, as a main component of clay mineral, is a better adsorbent of Cr, Zn, Cd and Pb than Fe₂O₃ in weathered and primary carbonate rocks. According to R-type clustering analysis, the main components of carbonate rock are divided into marine and continental sediments. Correlation analysis shows that heavy metal elements mainly exist in continental substances.

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Keywords: Carbonate rock; Heavy metal elements; Adsorbent; Enrichment

1. Introduction

Heavy metal elements in carbonate rocks [1–7] have been comprehensively studied, but there have been few systematic studies focused on heavy metals from primary carbonate rocks to weathered carbonate rocks and soil around them [8]. Although many factors can influence the enrichment of heavy metal elements, iron oxides, as the main adsorbent of heavy elements, are always the hot topics [9–19].

The present study focuses on the Lower Palaeozoic carbonate rocks in Beijing, to reveal migration and enrichment of heavy metal elements, such as Cr, Zn, Cd and Pb, by comparing the contents of those elements in primary

carbonate rocks, weathered carbonate rocks and soil coexisting with carbonate rock. Based on correlation analysis of heavy metal elements with Fe₂O₃ and FeO, the adsorptions of the heavy metals on iron oxides are compared. The enrichment of the heavy metals in primary carbonate rock is discussed on the basis of the correlations between heavy metal elements and major elements.

2. Geological setting and sampling

The carbonate rocks widely outcrop in the west and north of Beijing. Four profiles were selected: Shijiaying-Liulinshui, Huangtuling-Longmentai, Junzhuan-Xiawei-dian and Taizimu-Xiamaling in Fangshan and Mentougou, Beijing. The study strata are divided into two systems – Cambrian System (Changping, Mantou, Zhangxia and Chaomidian Formations) – and Ordovician System (Yeli, Liangjiashan and Majiagou Formations) according to

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“A Centenary Studies of Beijing Geology” [20]. In the study area, the carbonate rock strata strike NE, NNE or NEE, and the tectonic framework were mainly formed in the Yenshanian orogenic movements.

Carbonate rock samples were collected, including Cambrian and Ordovician rocks, and soil samples were collected above the carbonate rocks of the Zhangxia, Chaomidian, Yeli and Liangjiashan Formations (Table 1).

3. Analytical methods

Trace elements (Cr, Zn, Cd and Pb) were analyzed in primary carbonate rocks (fresh carbonate rocks), outer weathered carbonate rocks (weathered carbonate rocks) and soil samples coexisting with carbonate rocks. Only in carbonate rocks were major elements analyzed. The data are listed in Tables 1 and 2.

Samples were pulverized to ≤ 200 mesh. Element analyses of Shijiaying-Liulinshui and Huangtuling-Longmentai samples were carried out in the China National Research Center for Geoanalysis using the reported methods [21].

Major element analyses of Junzhuang-Xiaweidian and Taizimu-Xiamaling samples were carried out in the Institute of Geology and Geophysics of the Chinese Academy of Sciences. X-ray fluorescence (XRF) was used to determine the major elements. Sodium borate was used as flux to make fused beads that were prepared for each sample analyzed by XRF. The detection limit for TFe_2O_3 was 0.3%. FeO content was determined by potassium dichromate volumetry with detection limit 0.01%. The Fe_2O_3 contents in Tables 1 and 2 are the values obtained by subtraction of FeO contents from TFe_2O_3 .

Trace element analyses of Junzhuang-Xiaweidian and Taizimu-Xiamaling were carried out in the Institute of Geochemistry of the Chinese Academy of Sciences. The

Table 1
Samples collected and element contents.

Formation	Profile	Number	Lithology	Cd	Zn	Pb	Cr	Fe_2O_3	FeO	
Changping	Huangtuling-Longmentai	M37	Ashy dolomite	–	7.62	3.37	50.8	0.03	0.16	
Mantou	Huangtuling-Longmentai	S40 (inner)	Leutrite	0.01	29.7	10.6	30.5	3.96	0.42	
		S40 (outer)		0.05	29.4	19.3	30.9	4.1	0.31	
Zhangxia	Shijiaying-Liulinshui	S20 (inner)	Sparite	–	19.8	9.35	26.1	0.05	1.71	
		S20 (outer)		0.02	68.6	5.97	62.5	1.85	3.04	
		Soil 22	White soil	0.07	52.6	16.2	28.6	1.1	1.11	
		Soil 23	Yellow soil	0.15	83.4	75.1	101	3.86	2.05	
	Junzhuang-Xiaweidian	Soil 24	Black soil	0.14	77.3	45.3	68.5	2.81	2.6	
		M40	Limestone	–	7.26	8.42	3.23	1.27	1.21	
		M41	Limestone	–	30.3	28.9	11.6	1.37	1.00	
		M79	Sparry dolomite	0.01	16.8	14.4	5.78	0.41	0.36	
	Xiamaling-Taizimu	M92 (inner)	Limestone	0.02	22.3	15.5	3.01	0.29	0.28	
		M92 (outer)		0.03	20	77.1	15.5	3.77	0.93	
		M87	Sparite	–	6.78	9.11	4.33	0.91	0.49	
		Soil 16	Yellow soil	0.11	68.3	22.1	52.5	3.95	1.85	
Chaomidian	Huangtuling-Longmentai	M43	Sparite	0.05	39.1	22.5	35.4	0.5	1.69	
		M50 (inner)	Limestone	–	11.7	4.09	13.3	3.06	1.72	
	Junzhuang-Xiaweidian	M50 (outer)		0.05	49.1	76.9	3.66	0.69	0.22	
		Soil 13	Yellow soil	0.33	107	55.6	64.5	4.7	1.06	
Yeli	Shijiaying-Liulinshui	M24	Cryptite	–	10.3	4.29	17.7	0.03	1.45	
		M23	Calcarenite	–	45.3	4.62	49.3	0.32	4.36	
		S117	Micrite dolomite	–	9.96	2.16	3.44	0.34	0.37	
		Soil 111	Yellow soil	0.15	45.2	19.2	38.8	2.12	0.92	
	Junzhuang-Xiaweidian	M20	Cryptite	–	11.3	5.39	15.9	1.28	0.64	
Liangjiashan	Shijiaying-Liulinshui	M108	Sparite	–	4.43	2.13	3.82	0.14	0.05	
		S109 (inner)	Micrite dolomite	–	7.67	1.49	5.28	0.12	0.29	
		S109 (outer)		–	12.3	3.39	5.92	0.27	0.36	
	Huangtuling-Longmentai	S60	Cryptite	–	4.8	1.49	3.16	0.17	0.02	
		Soil 59	Grey soil	0.04	12.5	2.94	9.73	0.79	0.23	
		Soil 58	White soil	0.01	14	3	9.47	0.51	0.44	
		Soil 57	Black soil	0.12	38.1	9.25	31.6	3.03	0.21	
	Huangtuling-Longmentai	S16	Cryptite	0.25	37.5	17.5	21.5	2.28	1.35	
	Majiagou	Shijiaying-Liulinshui	S105 (inner)	Mud bearing Limestone	–	5.76	0.93	3.84	0.03	0.25
			S105 (outer)		0.01	7.86	1.63	6.64	0.43	0.16
Huangtuling-Longmentai		S63	Calcarenite	–	2.4	1.39	2.71	0.02	0.09	

The unit of trace element content is ppm, and for Fe_2O_3 and FeO contents the unit is wt%. Inner and no mark represent primary rock, outer represents weathered rock. The data for the Shijiaying-Liulinshui and Huangtuling-Longmentai samples are from the literature [21]; similarly in Table 2.

Table 2
Major elements of the Lower Palaeozoic carbonate rocks in Beijing (%).

	SiO ₂	TiO ₂	Al ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	FeO	Fe ₂ O ₃	LOI
S16	16.91	0.28	5.10	0.63	1.43	38.91	0.01	1.04	0.10	1.35	2.28	33.22
M20	10.41	0.23	2.94	0.03	1.86	43.95	0.11	1.94	0.04	0.64	1.28	36.57
M50 (inner)	7.55	0.23	1.54	0.07	2.77	44.46	0.01	0.83	0.10	1.72	3.06	38.67
M40	2.89	0.06	0.81	0.08	2.88	48.37	0.01	0.15	0.05	1.21	1.27	42.75
M41	2.09	0.04	0.67	0.25	3.62	48.86	0.01	0.12	0.03	1.00	1.37	42.18
M79	1.32	0.03	0.37	0.01	2.36	51.16	0.01	0.06	0.02	0.36	0.41	43.57
M87	2.10	0.03	0.56	0.06	1.45	51.63	0.01	0.07	0.03	0.49	0.91	42.48
M92 (inner)	0.65	0.01	0.16	0.01	1.51	53.12	0.01	0.00	0.02	0.28	0.29	43.56
M37	1.20	0.03	0.40	0.02	21.18	30.48	0.13	0.04	0.01	0.16	0.03	45.66
S40 (inner)	17.77	0.34	3.54	0.30	1.77	37.96	0.11	1.07	0.08	0.42	3.96	32.28
S20 (inner)	15.22	0.28	3.92	0.08	1.79	40.76	0.56	0.83	0.04	1.71	0.05	33.92
M24	8.11	0.24	2.43	0.03	2.04	46.02	0.18	0.74	0.03	1.45	0.03	38.51
M23	35.80	0.68	7.06	0.05	3.74	24.42	0.57	2.01	0.11	4.36	0.32	19.79
M108	1.90	0.03	0.56	0.01	0.70	54.16	0.01	0.09	0.02	0.05	0.14	42.40
S63	1.56	0.03	0.52	0.00	1.05	53.76	0.04	0.14	0.01	0.09	0.02	42.59
S105 (inner)	4.81	0.03	0.60	0.02	16.81	33.22	0.19	0.06	0.02	0.25	0.03	43.51
M43	17.74	0.28	5.02	0.34	3.22	36.72	0.32	1.32	0.11	1.69	0.50	31.68
S117	1.24	0.02	0.49	0.01	20.40	31.31	0.10	0.07	0.02	0.31	0.34	45.62

50 mg powdered carbonate rock samples were placed in a PTFE bomb [22] with 1 ml of HF and 1 ml of HNO₃. The sealed bomb was then heated in an electric oven at 195 °C for 20 h. After cooling, the bomb was opened, then 500 ng Rh, as an internal standard, was added and placed on a hot plate until the solutions evaporate to dryness. The final residue was diluted to 2000 times. The relative error of the analysis for the standard was <10%, and the relative standard deviation of the instrumental analysis was <5%.

4. Results and discussion

4.1. Results

The analytical results indicated that except for some abnormal samples, the contents of Cr, Zn, Cd and Pb were within the background value limits (Table 1) [23] in primary carbonate rock, and the contents of Cr, Zn, Cd and Pb in soil were lower than specified in soil environmental quality standard GB15618-1995 (China). The contents of Cr, Zn, Cd and Pb increased from primary carbonate rocks to weathered carbonate rocks and from primary carbonate rocks to the soil coexisting with the carbonate rocks (Fig. 1).

4.2. Discussion

According to the correlations between heavy metal elements and iron oxides, the migration and enrichment of Cr, Zn, Cd and Pb are considered as follows. The adsorptions of heavy metal elements on Fe₂O₃ and FeO are compared in different geologic media. On the basis of the correlations among different elements (except Cd, because the Cd content is lower than the detection limit in most samples), enrichment of the heavy metal elements in primary carbonate rock is discussed. As shown in Fig. 1, the distribution of Fe₂O₃ (ferric oxide) shows the same trend

as that of heavy metal elements in the samples, whereas the distribution of FeO does not have the same trend as that of the heavy metals.

To compare the adsorptions of heavy metal elements on Fe₂O₃ and FeO, the correlation coefficients of the heavy metals Cr, Zn and Pb with Fe₂O₃ and FeO were determined. The correlations between heavy metal elements and iron oxides in soil are apparent (Fig. 2). The correlation coefficient (*r*) of Zn with Fe₂O₃ is 0.76, and the *r* values for Cr and Pb with Fe₂O₃ are also >0.5. *r* for Cd with Fe₂O₃ is somewhat lower, but can also reflect the adsorption of heavy metal elements on Fe₂O₃. It is clear from these results that in soil, Fe₂O₃ plays an important role in adsorbing heavy metal elements, in accordance with previous reports [9–11,16]. The correlation coefficients <0.4 between heavy metal elements and Fe₂O₃ imply that Fe₂O₃ is not the main adsorbent of the heavy metals in weathered samples and primary rock samples.

The weaker correlations between heavy metal elements and Fe₂O₃ for rock samples may be related to the degree of weathering in weathered samples. At different stages of weathering, the adsorptions of heavy metals on Fe₂O₃ are different. Because of the low content of Fe₂O₃ (Fig. 1) in primary carbonate rock, the adsorption of heavy metal elements on Fe₂O₃ is reduced and no longer plays an important role. The correlation coefficients of FeO with Cr, Zn and Pb in soil and with Cr and Zn in weathered samples and primary samples are >0.59, which indicates that FeO plays an important role in adsorbing heavy metal elements. The correlation coefficients of FeO with Cd in soil, with Cd and Pb in weathered samples and with Pb in primary samples are <0.4, possibly because of competitive adsorption [24].

As shown in Fig. 2, iron oxides take an important role in adsorbing heavy metal elements. The adsorption of the heavy metals on Fe₂O₃ is greater than on FeO in soil.

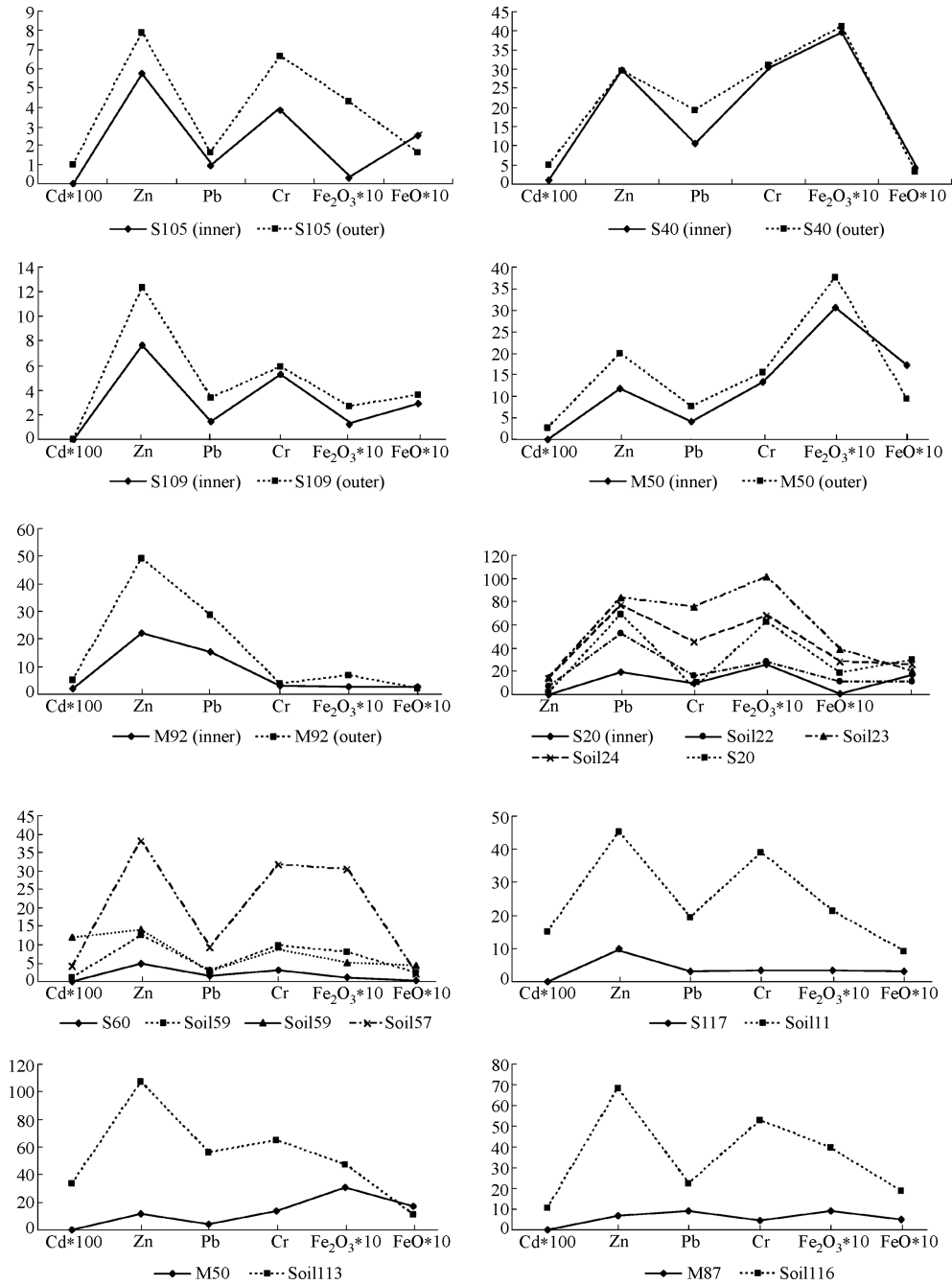


Fig. 1. Comparison of element contents of primary carbonate rocks, weathered carbonate rocks and soil above carbonate rocks. The unit is ppm for Cr, Zn, Cd and Pb.

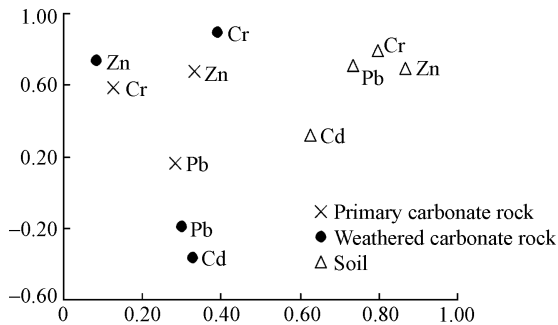


Fig. 2. Correlation of iron oxides with heavy metal elements.

Whereas the enrichment of Cr and Zn on FeO is greater than on Fe₂O₃ in primary and weathered carbonate rocks.

According to the R-type cluster analysis of major components and the correlation among different elements and based on analyzing the mutual relations of major components and their sediment source in primary carbonate rock, the enrichment of heavy metal elements is discussed in primary carbonate rock.

It can be seen from Fig. 3 that two types of components with negative correlation can be distinguished. The first type includes Al₂O₃, K₂O, SiO₂, Fe₂O₃, FeO, MnO and

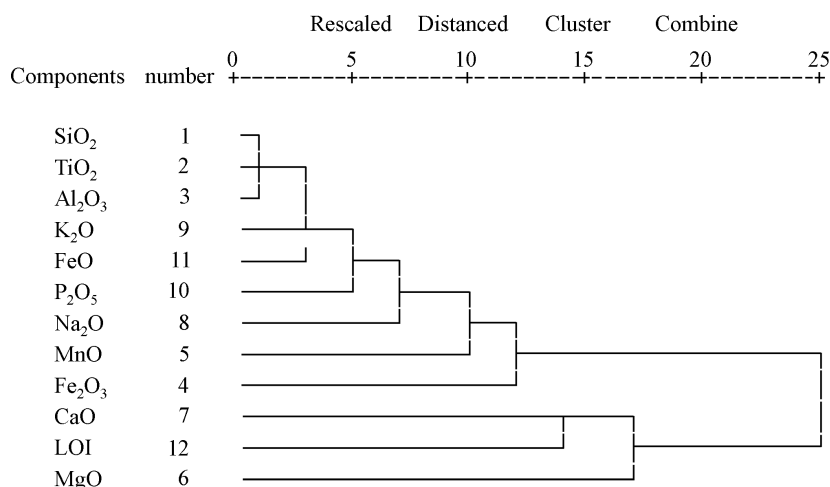


Fig. 3. R-type cluster analysis of major elements.

Na₂O; the second type includes CaO, MgO and LOI. In this classification, Mg–Ca components are emphasized; the other components exist in continental substances. On the basis of Fig. 3, we reach the following conclusions.

- (1) LOI has a positive correlation with CaO and has a negative correlation with SiO₂ ($r = -0.99$), which is a continental substance. This indicates that continental substances can inhibit the precipitation of carbonate rock mineral.
- (2) Al₂O₃ has a positive correlation with K₂O, FeO and TiO₂ and a negative correlation with CaO. These species occur mainly in continental clay: K is the main component of illite clay, and Fe and Ti are the main components adsorbed in clay minerals.
- (3) P₂O₅ has a positive correlation with K₂O, FeO, TiO₂ and Al₂O₃ and a negative correlation with CaO. According to the massive determination of geochemistry and marine chemistry [25], phosphorus is not unsaturated in the ocean and cannot precipitate directly by the way of inorganics from seawater. Thus, P should come mainly from continental substances.
- (4) The poor correlation of MnO with silicate components and negative correlation with MgO and CaO may relate to different structures of Fe or to partial entry of Mn into carbonate rock. It has been suggested that Mn exists mostly in dolomite crystals [26,27], but Fruth and Scherreiks [28] found that Mn was mainly controlled by the content of continental clay. Krumbein et al. [29] and Renard and Simanton [30] emphasized the controlling function of E_h and pH on the distribution of Mn [31].
- (5) The strong positive correlation of FeO with pelitic detritus indicates that the content of Fe is related to continental clay. The positive correlation of FeO with MnO shows that a reducing environment containing H₂S is beneficial to the precipitation of Mn and Fe.

It is clear from Fig. 4 that the correlations of Cr with Al₂O₃, SiO₂, FeO, K₂O, Na₂O, P₂O₅ and TiO₂ are strongly positive ($r > 0.6$), with CaO and LOI strongly negative ($r = -0.70, -0.65$), and with MgO weakly positive. These correlations indicate that the sedimentation of Cr is controlled by continental clay and enriched mainly in clay minerals, which are composed of Fe–Al silicate and phosphate minerals, the Cr content increases with the decrease in calcite content. The correlations of Zn with Al₂O₃, SiO₂, TiO₂, P₂O₅, K₂O, FeO and MnO are strongly positive ($r > 0.6$) and with MgO, CaO and LOI are significantly negative ($r = -0.27, -0.41$ and -0.78 , respectively). These correlations show that Zn exists mainly in clay minerals, phosphate minerals and MnO mineral of carbonate rock, and the enrichment of Zn is controlled by continental substances. Decline of Zn content accompanied by growth of the calcite and dolomite contents is also seen. The positive correlation ($r = 0.63$) with MnO arises because MnO is the main adsorbent of Pb. The negative correlation of Pb with CaO implies that part of the Pb may co-precipitate with calcite [32]. The weak positive correlations of Pb with SiO₂, TiO₂, Al₂O₃, P₂O₅, K₂O, FeO and Fe₂O₃ show that continental clay has little influence on sedimentation of Pb.

Pantsar-Kallio et al. [33] and Seaman et al. [34] pointed out that phosphate contributes to increasing the activity of Cr. Impellitteri [35] found that phosphate only adsorbs a little Zn. Consequently, phosphate minerals cannot be regarded as the adsorbent of Cr and Zn. The authors pointed out that the strong correlations of Cr and Zn with P₂O₅ are attributed to the symbiotic relationship of P₂O₅ with clay mineral in carbonate rock, and the clay mineral is the important adsorbent of Cr and Zn.

The negative correlations of the heavy metal elements with MgO and CaO can be interpreted as follows. First, the heavy metals are adsorbed mainly on clay mineral or MnO mineral. Secondly, the heavy metals may enter Ca or Mg lattice defects, then constitute metal carbonate [36]. In the present study, Cr, Zn and Pb showed signifi-

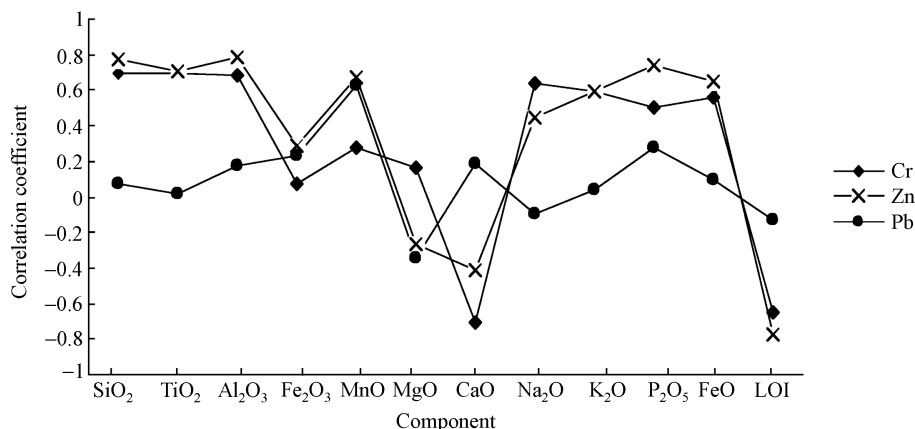


Fig. 4. The correlation of major elements with heavy metal elements.

cantly negative correlations with LOI, and CO₂ is the main component of LOI. That is to say, the decline of heavy metal element contents is accompanied by growth of calcite or dolomite. Thus, it is proposed that heavy metal elements adsorbed on the clay or MnO minerals lead to the negative correlations of the heavy metals with MgO and CaO. Continental substances are the main carriers of heavy metal elements.

According to the analysis above, during migration of heavy metal elements, only in soil can the Fe₂O₃ content cause the heavy metal element contents to change, so that Fe₂O₃ is not the dominant enrichment factor for the heavy metals. The enrichment of the heavy metals arises from the combined effects of several factors.

5. Conclusion

From primary carbonate rock to weathered carbonate rock and from primary carbonate rocks to the soil coexisting with carbonate rocks, the contents of the heavy metal elements Cr, Zn, Cd and Pb show increasing tendencies. In the course of weathering, the heavy metals were continuously accumulated.

In soil, Fe₂O₃ is one of the major factors affecting the enrichment of Cr, Zn, Cd and Pb, but in primary carbonate rock and weathered carbonate rock, the adsorptions of Cr and Zn on FeO are stronger than on Fe₂O₃. Continental clay is the main adsorbent of Cr and Zn, and continental MnO is the main adsorbent of Pb. Overall, continental substances are the major carriers of heavy metal elements in primary carbonate rock.

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