

Chemical Forms of Heavy Metals in Carbonate-Derived Laterite and Enrichment of Its Iron Oxide Minerals*

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Abstract: In this paper the seven-step continuous extracting method was employed in the study of chemical forms of the six heavy metals Co, Zn, Pb, Cu, Cr and Mn. The result shows that the metals in the laterite are present in the chemical form of crystalline iron oxides and residues, and they are transformed toward organic and exchangeable forms in the surface soil. Linear regression analysis indicates that the above heavy metals have a positive correlation with the crystalline iron oxide minerals. The crystalline iron oxide minerals have a very important role to play in the enrichment of heavy metals, especially the solid components in the laterite.

Key words: laterite; chemical forms of heavy metals; iron oxide mineral

The formation and evolution of carbonate-derived laterite involves such pedogenetic geochemical processes as Si-Al enrichment, Ca-Mg depletion, Fe-Mn enrichment and Al enrichment and Si depletion. In the processes mentioned above the heavy metals Co, Zn, Pb, Cu, Cr and Mn have experienced significant enrichment and differentiation, exhibiting different ecological effects (Zhu Lijun et al., 1996). However, as heavy metals in the supergene environment are often present in different chemical forms, they are different in effectiveness and toxicity toward organisms. This cannot be explained merely in terms of the total amount of the metallic elements. In this paper the seven-step continuous extracting method was employed to distinguish the chemical forms of the heavy metallic elements in the laterite with an attempt to reveal the forms of combination of the heavy metallic elements with the solid components in the laterite and ascertain the influence of iron oxide minerals on the transport, enrichment and transformation of the heavy metals.

Samples and Method

From the geological point of view, the laterite discussed in this study refers to the Quaternary red weathering crust developed on limestones and dolomites as well as their transitional rock type—carbonate rocks. The samples were collected from the Anshun dolomite-derived laterite section which is possessed of typical subtropical karst geomorphological, hydrological and eco-environmental features in the karst areas of Guizhou Province. The geology, geochemistry and mineralogy of the laterite samples have been well documented by the senior author (Zhu Lijun et al., 1996). At the same time, the samples were analyzed for the total amount of Co, Zn, Pb, Cu, Cr and Mn in clay minerals and iron oxide minerals.

As for the identification of chemical forms of heavy metallic elements, the method of Stover (1976) is more commonly used in the field of environmental chemistry and that of Tessier (1979) and Shuman (1985), as well as the form-grading system developed on this basis, in the fields of soil chemistry and environmental geochemistry. On the basis of the achievements made in recent years both at home and abroad in the study of how to distinguish the chemical forms of heavy metallic elements by using the seven-step continuous extracting method, in combination of the geochemical characteristics of carbonate-derived laterite, the chemical forms of heavy metals in the laterite are identified by using the seven-step continuous extracting method as described in Table 1. The contents of heavy metals of different chemical forms were analyzed by ICP spectrometry.

Table 1. Multi-element ICP spectrometric analysis and seven-step continuous extracting procedure

Step	Form	Extracting agent	Soil/liquid ratio	Condition
I	Exchangeable	1 mol/L Mg(NO ₃) ₂ (pH 7.0)	2.50 g/10 mL	Vibrating for 2h at 25°C
II	Carbonate-combined	1 mol/L NH ₄ Ac (pH 5.0)	2.50 g/25 mL	Vibrating for 2h at 25°C
III	Amorphous Mn oxide-combined	0.1 mol/L NH ₂ OH·HCl (pH 2.0)	2.50 g/25 mL	Vibrating for 1 h at 25°C
IV	Organic	a. 30% H ₂ O ₂ , added twice, totaling 30 mL, evaporizing till dryness b. 1 mol/L NH ₄ Ac(pH 5.0)	2.50 g/25 mL	a. Water bathing till dryness and then cooling b. Vibrating for 2h at 25°C
V	Amorphous iron oxide-combined	0.2 mol/L H ₂ C ₂ O ₄ + 0.2 mol/L (NH ₄) ₂ C ₂ O ₄ (pH 3.0)	2.50 g/50 mL	Vibrating for 4 h at 25°C in the dark
VI	Crystalline iron oxide-combined	0.2 mol/L H ₂ C ₂ O ₄ + 0.2 mol/L H ₂ C ₂ O ₄ + 0.11 mol/L Vc (pH3.0)	2.50 g/50 mL	Water bathing for 1 h at 96°C
VII	Residual		HF - HClO ₄	Digesting

(After Shao Xiaohou, Xin Guangxi and Hou Wenhua, 1994)

Chemical Forms of Heavy Metals in the Laterite

As illustrated in Table 1, the heavy metals in the laterite can be distinguished into the following chemical forms by using the seven-step continuous extracting method: exchangeable, carbonate-combined, amorphous Mn oxide-combined, organic, amorphous iron oxide-combined, crystalline iron oxide-combined and residual. The contents of heavy metals of different chemical forms analyzed by ICP spectrometry and their distributions are presented in Table 2. From Table 2 we can see the following features:

(1) *Exchangeable (EXC) and organic (OM) forms* the six heavy metals Co, Zn, P., Cu, Cr and Mn in the laterite are present in the exchangeable and organic forms and their contents are relatively low, but they are precisely increased in the surface soil.

(2) *Carbonate-combined form (CARB)* Although laterite is genetically connected with the weathering of carbonate rocks in the karst environment, the heavy metals Co, Zn, Pb, Cu, Cr and Mn in it are not obviously incorporated into carbonate. Therefore, the contents of carbonate-combined heavy metals are lowest, occupying a minimal proportion of the total.

Table 2. The contents of heavy metals of the various chemical forms in the laterite developed from carbonate rocks in Guizhou Province ($\times 10^{-6}$)

Element	Section type	Sample (sampling depth; m)	Exchangeable (EXC)	Carbonate-combined (CARB)	Organic (OM)	Amorphous Mn oxide-combined (OX)	Amorphous Fe oxide-combined (AFe)	Crystalline Fe oxide-combined (CFe)	Residual (RES)
Co	Dolomite-derived laterite, Anshun	Layer A of surface soil (0.2)	0.24	0.10	1.23	1.56	2.49	2.05	13.7
		Layer B of surface soil (0.5)	0.56	0.15	1.60	1.11	2.78	2.18	12.6
		Laterite (1)	0.08	0.05	0.54	0.35	0.59	4.22	26.7
		Laterite (3)	0.16	0.02	0.49	9.33	3.53	5.13	22.8
		Laterite (5)	0.32	0.15	1.53	11.0	4.24	2.83	18.7
		Laterite (8)	0.12	0.46	0.82	64.3	3.93	3.23	15.9
Zn	Dolomite-derived laterite, Anshun	Layer A of surface soil (0.2)	3.36	0.02	3.53	3.16	4.40	15.9	125
		Layer B of surface soil (0.5)	0.96	0.06	2.96	1.06	4.70	16.0	131
		Laterite (1)	1.24	0.30	1.00	1.15	4.44	12.2	149
		Laterite (3)	0.40	0.01	1.95	0.97	7.25	48.8	171
		Laterite (5)	0.44	0.08	1.52	1.41	3.93	22.20	243
		Laterite (8)	0.20	0.31	1.07	4.52	6.06	29.50	185
Pb	Dolomite-derived laterite, Anshun	Layer A of surface soil (0.2)	1.24	0.97	8.91	2.16	33.20	33.40	78.5
		Layer B of surface soil (0.5)	1.28	0.34	9.98	2.00	31.70	34.20	79.2
		Laterite (1)	0.40	0.29	6.02	4.27	17.10	46.10	119
		Laterite (3)	0.32	0.01	4.89	9.12	37.20	63.90	99.0
		Laterite (5)	0.64	1.04	6.84	1.04	42.40	45.20	102
		Laterite (8)	10.28	15.50	32.50	50.6	55.60	69.80	90.3
Cu	Dolomite-derived laterite, Anshun	Layer A of surface soil (0.2)	0.048	0.03	4.47	0.07	6.87	10.2	56.8
		Layer B of surface soil (0.5)	0.096	0.32	3.49	0.03	6.88	9.75	56.9
		Laterite (1)	0.032	0.01	1.20	0.41	4.91	15.4	70.7
		Laterite (3)	0.012	0.26	1.51	0.50	6.73	21.6	80.8
		Laterite (5)	0.024	0.28	1.44	0.53	6.36	20.9	93.5
		Laterite (8)	0.24	2.91	3.44	7.46	6.08	39.6	98.1
Cr	Dolomite-derived laterite, Anshun	Layer A of surface soil (0.2)	0.48	0.28	7.33	0.08	2.86	30.3	58.2
		Layer B of surface soil (0.5)	0.6	0.26	7.41	0.05	2.83	27.5	60.6
		Laterite (1)	0.24	0.42	1.01	0.22	5.09	47.1	70.8
		Laterite (3)	0.28	0.64	2.06	0.34	3.61	52.1	69.5
		Laterite (5)	0.32	0.41	1.29	0.28	4.31	50.1	68.0
		Laterite (8)	0.40	0.96	0.89	1.76	2.07	33.4	72.6

Table 2. (continued)

Element	Section type	Sample (sampling depth; m)	Exchangeable (EXC)	Carbonate-combined (CARB)	Organic (OM)	Amorphous Mn oxide-combined (OX)	Amorphous Fe oxide-combined (AFe)	Crystalline Fe oxide-combined (CFe)	Residual (RES)
Mn	Dolomite-derived laterite, Anshun	Layer A of surface soil (0.2)	11.2	7.82	27.6	67.9	25.4	38.4	81.1
		Layer B of surface soil (0.5)	34.8	13.0	46.8	47.1	28.6	45.6	91.3
		Laterite (1)	4.86	0.99	26.3	9.27	4.20	32.3	102
		Laterite (3)	6.04	1.67	4.17	2.21	11.4	67.7	171
		Laterite (5)	14.8	4.39	89.7	22.4	35.2	107	226
		Laterite (8)	0.43	0.24	66.9	11.0	40.1	59.8	89.9

(3) *Amorphous Mn oxide-combined form (OX)* The content of Co, which is present in the amorphous Mn oxide-combined form, is relatively high in the middle and lower parts of the laterite section, indicating that some affinity between Co and Mn at the rock/soil interface (weakly alkaline and weakly oxidized) in the middle and lower parts of the laterite section. But Mn, which is present in the amorphous Mn oxide-combined form, is low in content, generally accounting for less than 10% of the various chemical forms of heavy metals.

(4) *Amorphous iron oxide- (AFe) and crystalline iron oxide-combined (CFe) forms*

These two forms of heavy metals account for a large portion of the total in the laterite, with the latter significantly larger than the former. This suggests that there is an obvious geochemical affinity between iron oxide minerals and Co, Zn, Pb, Cu, Cr and Mn in the laterite. These heavy metals are those mineralogically referring to the equivalents isomorphously present in the lattice of iron oxide minerals or adsorbed on them.

(5) *Residual form (RES)* The so-called residual form refers to those heavy metals which are tightly bound in the lattice of other minerals (mainly silicate and sulfide minerals) and cannot be extracted by the agents which are powerful enough to extract Co, Zn, Pb, Cu, Cr and Mn. In the laterite the heavy metals Co, Zn, Pb, Cu, Cr and Mn present in the residual form are highest in content. With a few exceptions (e.g. Co at the depth of 8 m in the bottom of the laterite section), they account for more than 50% of the various chemical forms respectively, especially Zn which accounts for more than 70%.

(6) *The six heavy metals Co, Zn, Pb, Cu, Cr and Mn in the laterite* They are present mainly in the residual and crystalline iron oxide-combined forms, and the contents of those heavy metals that are present in the exchangeable and organic forms and are easy to absorb and utilize by organisms are extremely low. Some of them are even seriously depleted (e.g. Cu, Zn). As the heavy metals present in the residual form are highly stable, they are not only uneasy to absorb or utilize by organisms, but also hard to migrate and become enriched. Therefore, the newly produced components during the weathering-pedogenesis of laterite, for example crystalline iron oxide minerals, can play a decisive role in the mobilization, migration and enrichment of the heavy metals in the laterite section.

The Role of Iron Oxide Minerals on the Enrichment of Heavy Metals

Iron oxide minerals are an important mineral component and structural unit of carbonate-

derived laterite. Because there are generally no iron oxide minerals or only minor amounts are present in parental carbonate rocks, iron oxide minerals are usually newly formed minerals during the weathering-pedogenesis of laterite, which are characterized by small grain size, big specific surface area and strong adsorbing capacity. The minerals are possessed of special absorbing capability toward some heavy metals, thus exerting a direct influence on the geochemical behavior and cycling character of heavy metals in the laterite (Zhu Lijun et al., 1995, 1996, 1997). In order to ascertain the correlation between iron oxide minerals and heavy metals in the laterite on the quantitative basis, correlation analysis has been made for crystalline iron oxide minerals, amorphous iron oxide (amorphous compounds) and the heavy metals Cu, Zn, Pb, Co, Cr and Mn which are present in the crystalline iron oxide- and amorphous iron oxide-combined forms. The result shows that these six heavy metals are positively correlated with the crystalline iron oxide minerals. The multivariant regression equation is given below:

$$\begin{aligned} \text{Crystalline iron oxide mineral} = & 1.206518 + 0.3581588 \text{ Co} - 0.00251 \text{ Zn} \\ & + 0.00325 \text{ Pb} + 0.0611 \text{ Cr} + 0.000384 \text{ Cu} - 0.00182 \text{ Mn} \\ [r (\text{correlation coefficient})] = & 0.984 \end{aligned}$$

It is evident that the most obvious correlation is noticed between the heavy metals Cr, Pb and Co and crystalline iron oxide minerals with the correlation coefficients being 0.943, 0.775 and 0.751, respectively. However, the poorest correlation is evidenced between the six heavy metals and amorphous iron oxide with the correlation coefficient being 0.5.

The remarkable correlation between the iron oxide minerals in the laterite and the heavy metals Cr, Pb and Co quantitatively reflects the role of iron oxide minerals in the enrichment of heavy metals. Recent studies by the authors on the surface chemical properties of iron oxide minerals and the mechanism of adsorption of elements on them provide strong evidence suggesting that iron oxide minerals in the laterite are the major carriers of the heavy metals Co, Pb, Zn, Cr and Cu and their capability of enriching the metals tends to increase with the pH value of laterite (Zhu Lijun et al., 1996, 1997).

The Influence of Weathering-Pedogenesis on Comparative Analysis of the Chemical Forms of Heavy Metals

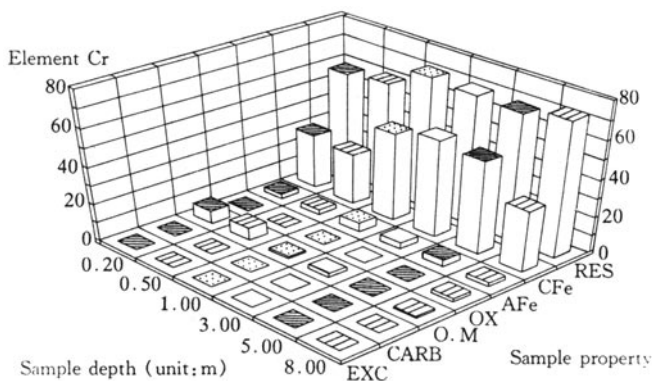


Fig. 1. The chemical forms of the heavy metal Cr in the laterite profile.

At a glance of Table 2 and Fig. 3, it is clearly seen that the variations of heavy metals of various chemical forms with depth in the laterite profile reflect the influence of weathering-pedogenesis on the chemical forms of heavy metals. To further understand the influence and eco-environmental effect of weathering-pedogenesis, particularly organism-involved pedogenesis of the surface layer of laterite, on the chemical forms of heavy metals, we go into details on the relative differentiation and enrichment of heavy metals of the various chemical

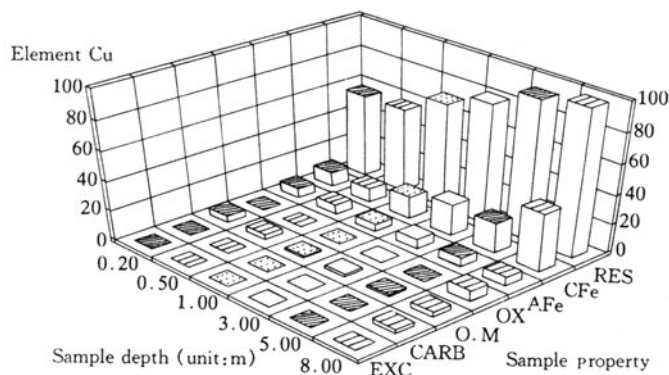


Fig. 2. The chemical forms of Cu in the laterite profile.

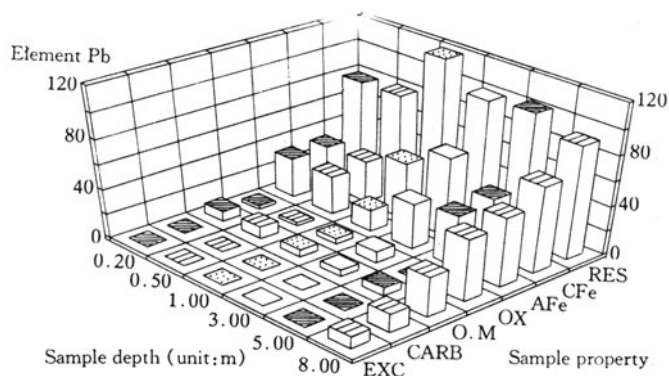


Fig. 3. The chemical forms of Pb in the laterite profile.

matter and the decrease of pH have led to the lowering of capability of adsorbing heavy metals by iron oxide minerals. In addition the dissolution and conversion of some of the iron oxide minerals have made the heavy metals adsorbed on the iron oxide minerals or present in the crystalline iron oxide-combined form changed into those of organic or exchangeable form. From this it can be seen that the influence of weathering-pedogenesis of laterite on the chemical speciation of heavy metals is actually exerted by iron oxide minerals produced during the weathering-pedogenetic processes.

Summary

1. The six heavy metals Co, Zn, Pb, Cr, Cu and Mn contained in the carbonate-derived laterite of Guizhou Province are present dominantly in the crystalline iron oxide-combined and residual forms. The contents of Co, Zn, Cu and Mn present in the exchangeable and organic forms in the surface layer of laterite are relatively increased.

2. Solid components, particularly those crystalline iron oxide minerals, in the laterite show a strong tendency to enrich the heavy metals Co, Zn, Pb, Cu, Cr and Mn. There is a re-

forms. Listed in Table 3 are the calculated values for the surface soil. In combination with Tables 2 and 3, it can be seen that with the sustained development of weathering-pedogenesis of laterite, especially in the case of involvement of living organisms on the earth's surface, the chemical weathering of the surface layer of laterite has developed into a geochemical process dominated by bioweathering-pedogenesis, accompanied with the production of organic matter in large amounts. For this reason, the physicochemical micro-environment of the surface layer of laterite has been changed. Based on the measured results by the authors, the content of organic matter in the surface layer of laterite is generally within the range of 3% - 5% while that in the whole weathered layer is mostly within the range of 0.5% - 0.1%, or even lower. The pH value of surface soil is generally within the range of 4 - 5 while that of the whole weathered layer, 6 - 7, even higher (Zhu Lijun et al., 1996, 1997). The increase of organic

markable correlation between Cr, Pb and Co and the crystalline iron oxide minerals.

Table 3. Characteristic values (%) of relative enrichment (+) or differentiation (-) of heavy metals of the various chemical forms in the surface-layer soil of Anshun dolomite-derived laterite profile

Element	Strat. position	Exchangeable	Carbonate-combined	Organic	Amorphous Mn oxide-combined	Amorphous Fe oxide-combined	Crystalline Fe oxide-combined	Residual
Co	Layer A of surface soil	-3.2	-35.5	+18.8	-89	-5.6	-37.3	-25.5
	Layer B of surface soil	-125.8	-3.2	+54.6	-92	+5.3	-33.3	-31.5
Zn	Layer A of surface soil	+205.5	-84.6	+76.5	+54	-14	-33.8	-25.2
	Layer B of surface soil	-12.7	-53.8	+48	-48	-8.4	-33.3	-21.6
Pb	Layer A of surface soil	+44.2	-67.9	-22	-81	-8.3	-31.5	-17.5
	Layer B of surface soil	+48.8	-88.7	-13	-82.6	-12.4	-29.8	-15.9
Cu	Layer A of surface soil	-36	-95.3	+72.6	-95.6	+9	-47.2	-25.3
	Layer B of surface soil	+28	-50	+34.8	-98	+9.1	-50	-25.2
Cr	Layer A of surface soil	+26	-43.4	+120	-82	-17	-24	-12.3
	Layer B of surface soil	+58	-47.5	+122.5	-89	-18	-31	-9.6
Mn	Layer A of surface soil	-4	+65	-35	+12	+5	-34	-35.6
	Layer B of surface soil	+195	+176	+8.8	-21	+18	-22	-27.8
Fe	Layer A of surface soil	+11.5	+7	+457	-24	+1522	-25.3	-30
	Layer B of surface soil	+175	+71	+428	-14	+119	-22.9	-24.9

Equation for calculating the characteristic values:

$$\frac{\text{The content of element of a certain chemical form in the soil of surface layer} - \text{the average content of the element in this chemical form in the laterite}}{\text{the average content of the element in this chemical form in the laterite}} \times 100\%$$

Enrichment (+); differentiation (-).

3. The enrichment of heavy metals by iron oxide minerals in the laterite always occurs in the weathering-pedogenetic environment with a pH value of 6–7. With increasing pH value, the tendency of heavy metal enrichment becomes stronger and stronger. With the sustained development of soil weathering at the surface layer of laterite, plenty of organic matter will be produced, and the formation and conversion of iron oxide minerals have led to the change of surface-layer micro-environment in the laterite profile, thus making the chemical forms of some heavy metals change with the conversion of iron oxide minerals. As a result, the contents of heavy metals of effective or organic forms in the surface layer of laterite are increased. As the bio-effectiveness and toxicity of heavy metals in soils chiefly depend on how much they are present in the organic and exchangeable forms. Therefore, the formation and conversion of iron oxide minerals in the surface layer of laterite could exert a direct influence on the formation and conversion of the chemical forms of heavy metals. To some extent, it can also control the fertility and pollution state of laterite.

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