

Geochemical translocation of trace metals in iron-manganese cutans and matrices of subtropical soils in China

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Abstract

The geochemical translocation of trace elements in iron-manganese cutans and the corresponding matrix soils of Fragiudalfs (FRA), Ferrudalfs (FER) and Hapludult (HAP) in Subtropical China, were subjected to selective dissolution with 0.1 mol/L $\text{NH}_2\text{OH}\cdot\text{HCl}$ (HAHC) and dithionite-carbonate-citrate (DCB) solutions, respectively. The MnO_2 , Fe_2O_3 , Ba, Co, Pb, Li, Cu, Zn, Ni, Cd contents in iron-manganese cutans are notable higher than those in corresponding matrix soils. Iron contents extracted by HAHC solutions is less than 3% of that by aqua regia solution, but the extractable manganese contents is over 80% in cutans. The Ba, Zn, Cd, Co, Cu, Ni and Pb mainly enrich in manganese minerals, and majority of Cr, Li and Mo exist in iron minerals of cutans. Selective extraction shows that the trace elements translocated from matrix soils and enriched in cutans along with the illuviation of iron- and manganese oxides during the formation of cutans.

Key Words

Geochemical translocation, iron oxide, iron-manganese cutan, manganese oxide, matrix soil, trace metal.

Introduction

Trace metals have different geochemical actions in the process of mineral weatherings and soil developments. The translocation abilities of trace metals in soils are different due to the diversity of properties among elements (Galán *et al.* 2008). Soil iron-manganese cutan is product of movement and precipitation of the special soil materials, such as iron and manganese oxides and clays (Brewer 1976). It could enrich lots of trace metals (Jongmans *et al.* 1996; Manceau *et al.* 2007). Their special material compositions reflected the geochemical information of elemental migration, deposition and transformation in the soil-forming process, and indicated the new combination and existing form of trace elements after translocation and transformation from bulk soils (Sullivan and Koppi 1993; Liu *et al.* 2002). Iron-manganese cutans are widely distributed in Alfisols and Ultisols in subtropical area in China. Although base ions are massively leached, the iron-manganese oxides and other trace metals are in the stage of frequent migration and deposition (Huang *et al.* 2007, 2008). Therefore, this article analysed the composition of iron and manganese oxides of the iron-manganese cutans in the Alfisols and Ultisols, studied the translocation characteristic of trace elements in the cutans, and gained the geochemical relationship between these trace elements and iron and manganese oxides of iron-manganese cutans in these subtropical Chinese soils.

Methods

Three representative soils with iron-manganese cutans in B horizons from different subtropical regions in central China, were collected for this study. They are Fragiudalf, Ferrudalf and Hapludult, according to Key to Soil Taxonomy (Soil Survey Staff, 2006), from Xinyang city in Henan Province, Wuhan City in Hubei Province and Taoyuan City in Hunan Province, respectively. There were collected 54 soil samples from the three pedons for physicochemical and statistical analyses. These soils were all from barren lands on the upper part of slopes in hilly area with good drainage conditions. The subangular blocky ped (matrix soils) containing cutans were collected from the B horizon at the depth about 20-50 cm. The cutan samples were black or brown materials collected lightly with a sterile blade under a microscope from soil blocks. Matrix soils (i.e., at least 25-30 kg) were sampled from adjacent ped interior blocks that were scraped off cutans. The air-dried matrix soils and cutans were ground to pass 10-, 20-, 60- and 100-mesh sieves, respectively. Table 1 is shown the climatic data and description of the selected sample tested. The cutan samples were dissolved in 0.1 mol/L $\text{NH}_2\text{OH}\cdot\text{HCl}$ (HAHC) at pH 3.0 with a sample weight/ solution volume ratio of 1:100 to selectively reduce and dissolve manganese oxides in samples, and shaken at 25°C for 2 h (Tokashiki *et al.* 1986). The supernatant was collected after centrifugation for analysis. The total elements (Fe, Mn, Cu, Zn, Co, Pb, Li, Cr, Cd, Ni, Mo, Ba) were determined by Varian Vista-MPX ICP-OES, after acid digestion with aqua regia (HNO_3 : HCl = 1:3) (125°C). Samples were extracted with dithionite-carbonate-citrate (DCB)

(Mehra and Jackson 1960) and HAHC to determine free Fe-oxide (Fed) bound and iron-manganese oxide bound metals, respectively.

Table 1. Climate data and description of the selected samples tested.

No.	Sample	Location	Parent material	MAR ^A mm	MAT ^B °C	SM & TR ^C	Description
1-C	Cutan of FRA ^D	Xinyang (32°22'N, 114°39'E)	Quaternary (Q ₃)	670	12.8-15.5	Udic-mesic	Reddish black moist color (10R 2/1)
1-B	Matrix of FRA						Strong brown (7.5YR 5/6); light clay; weak/moderate subangular blocky structure; very firm; some cutans
2-C	Cutan of FER ^E	Wuhan (30°42'N, 114°24'E)	Quaternary (Q ₃)	1269	15.8-17.5	Udic-thermic	Yellowish block moist color (5Y 2/1)
2-B	Matrix of FER						Yellowish red (5YR 5/8); clay; weak/moderate subangular blocky structure; very firm; many cutans
3-C	Cutan of HAP ^F	Taoyuan (28°52'N, 111°27'E)	Quaternary (Q ₂)	1437	16.0-16.5	Udic-thermic	Reddish black moist color (10R 2/1)
3-B	Matrix of HAP						Reddish yellow (7.5YR 6/8); clay; moderate subangular blocky structure; very firm; many cutans

^AMAR = Mean annual rainfall; ^BMAT = Mean annual temperature; ^CSM&TR = Soil moisture and temperature regime; ^DFRA = Fragiudalf; ^EFER = Ferrudalf; ^FHAP = Hapludult.

Results

The basic properties and HAHC-extracted iron and manganese of cutan and matrix

The pH, organic matter (O.M.), base saturation (B.S.), Fe₂O₃, MnO₂, and clay contents of cutans are higher than that of matrix soils in horizon B (Table 2). Especially the MnO₂ contents in the iron-manganese cutans are 8.83-19.31 times higher than that in the relevant matrix soils. This indicates that iron-manganese cutans of Fragiudalf, Ferrudalf and Hapludult contain more clay, organic matter and iron-manganese oxides than the corresponding matrix soils. Vermiculite, illite and kaolinite are the major clay compositions in both cutans and matrix soils. Hydroxy-interlayered vermiculite (HIV) exists in matrix soils of Fragiudalf and Ferrudalf. Goethite is the main Fe-oxide mineral in cutans and matrix soils. Low amounts of birnessite and lithiophorite are present in cutans, but they cannot be detected in corresponding matrix soils (Huang *et al*, 2007, 2008).

Table 2. Selected soil chemical and physical properties.

No.	pH ^a	O.M. ^b g/ kg	B.S. ^c %	Fe ₂ O ₃ g/ kg	MnO ₂ g/ kg	Clay g/ kg	Mineralogy of samples (Huang <i>et al</i> , 2007, 2008)	
							Clay mineralogical composition ^d	Fe and Mn oxides ^e
1-C	6.70	18.01	50.02	57.96	16.41	526.4	V(++), I(+++), K(+)	G, B, L
1-B	6.54	12.70	55.74	48.63	0.94	424.0	V(++), H(+), I(+++), K(++)	G
2-C	5.93	3.35	45.06	62.37	10.04	514.8	V(++), I(+++), K(++),	G, B, L
2-B	5.81	3.01	53.65	45.56	0.52	457.7	V(+), H(+), I(+++), K(++)	G
3-C	4.41	3.61	35.85	60.76	5.83	547.8	V(+), H(+), I(+++), K(++)	G, B, L
3-B	4.25	3.24	34.15	56.53	0.66	462.5	V(+), H(+), I(+++), K(++)	G

^a Soil:H₂O = 1:2.5. ^b O.M. = organic matter. ^c B.S. = base saturation. ^d V = vermiculite, H = hydroxy-interlayered vermiculite (HIV), I = illite, K = kaolinite. Symbols of +: <100 g/ kg, ++: 100-250 g/ kg, +++: 250-500 g/ kg, ++++: 500-750 g/ kg. The semiquantitative mineralogical compositions were estimated by peak areas of XRD to phyllosilicate. ^e G = goethite, B = birnessite, L = lithiophorite.

Table 3. Manganese and iron oxides extracted by HAHC solutions.

No.	Fe ₂ O ₃			MnO ₂		
	Total content g/ kg	HAHC-extracted g/ kg	% extracted	Total content g/ kg	HAHC-extracted g/ kg	% extracted
1-C	57.96	1.40	2.42	16.41	13.69	83.42
2-C	62.37	1.56	2.50	10.04	10.01	99.70
3-C	60.76	1.27	2.09	5.83	5.08	87.14

The iron-manganese cutans were treated with 0.1mol/L HAHC solution at pH 3.0 (Table 3). The iron extracted by HAHC is less than 3% of that by aqua regia solution, but the extractable manganese is over 80%. This indicates that HAHC selectively reaction with Mn is stronger than that of Fe. Thus, it can extract the

majority of manganese from iron-manganese cutans.

The form of trace metals in cutan and matrix after different selective dissolution

Compared with the matrix soils, the cutans enrich in trace elements (excepted Cr and Mo) (Table 4). This shows that a great deal of the trace elements move out of matrix soils and deposit in iron-manganese cutans. The contents of Ba, Co and Pb in cutans are especially higher than those in matrices. Ba, Zn, Cd, Co, Cu, Ni and Pb dissolve with HAHC in cutans are notably higher than those in the corresponding matrices that indicate these metals mainly enrich in Mn-oxides. Cr, Li and Mo dissolve in HAHC are obviously lower than those extracted with DCB and aqua regia solutions in cutans. Thus, Cr, Li, and Mo elements mainly exist in Fe-oxides in cutans.

Table 4. The contents of trace metals dissolved with aqua regia, HAHC and DCB solutions.

Sample	Ba (µg/g)			Zn (µg/g)			Cd (µg/g)			Co (µg/g)		
	AR ^A	HAHC ^B	DCB ^C	AR	HAHC	DCB	AR	HAHC	DCB	AR	HAHC	DCB
Cutan	156.73	67.49	98.73	51.07	2.17	30.10	0.45	0.06	0.21	11.90	7.44	9.44
Matrix	436.23	366.74	421.95	68.97	58.98	66.08	0.79	0.47	0.59	166.43	125.38	164.71

Sample	Cr (µg/g)			Cu (µg/g)			Li (µg/g)		
	AR	HAHC	DCB	AR	HAHC	DCB	AR	HAHC	DCB
Cutan	21.91	1.34	14.48	27.33	1.41	4.22	18.57	3.49	4.95
Matrix	15.31	0.20	10.04	41.35	28.53	34.72	21.61	7.48	18.05

Sample	Mo (µg/g)			Ni (µg/g)			Pb (µg/g)		
	AR	HAHC	DCB	AR	HAHC	DCB	AR	HAHC	DCB
Cutan	2.26	0.20	1.60	26.34	1.32	5.08	7.82	5.66	6.47
Matrix	1.78	0.20	1.14	47.43	27.51	40.21	124.30	106.85	119.37

^AAR = aqua regia extraction; ^BHAHC = 0.1 mol/L NH₂OH·HCl extraction; ^CDCB = dithionite-carbonate-citrate extraction.

The molar ratio of trace metals in cutans and matrix soils

The metals respectively in the pairs of Mn and Fe, Cu and Zn, Zn and Cd, Co and Ni, Pb and Co have shown the similar chemical behaviors, and the mean molar ratios of those elements are listed in Table 5. The molar ratios of Mn/Fe, Cu/Zn, Co/Ni and Pb/Co in cutans all are greater than those of the matrices, but Zn/Cd molar ratio is shown the reversed trend. This indicates that Mn, Cu, Co, Pb and Cd are easy to translocate in soils and deposit in cutans, respectively. Molar ratios of Mn to Fe and Co to Ni in cutans are respective 8.00 and 7.80 times higher than those in matrices, and the molar ratios of Cu/Zn, Zn/Cd and Pb/Co in cutans are respective 1.11, 0.77 and 1.14 times higher than those in matrices. It indicates that the differentiations of Mn and Fe, Co and Ni between cutans and matrices are greater than those of Cu/Zn, Pb/Co and Zn/Cd, respectively.

Table 5. The molar ratios of some trace metals in cutans and matrix soils.

Sample	Mn/Fe	Cu/Zn	Zn/Cd	Co/Ni	Pb/Co
Cutan	0.08	0.60	87.30	3.51	0.75
Matrix	0.01	0.54	113.49	0.45	0.66

The standard redox potential (Eh°) of manganese system is generally higher than that of the iron system, such as Eh° is 1.23 V for MnO₂-Mn (□) system and 0.77 V for Fe (□)-Fe (□) system (McKenzie 1989; Huang 1991). Therefore, manganese is generally more sensitive than iron to the change of wetting and drying. This led that the molar ratio of Mn to Fe in cutan is higher than that of matrix soil. MnO₂ contents show positive correlation with Co (R=0.72, n=54) and Ni (R=0.55, n=54) in matrices (Table 5). In cutans, the correlation of Ni and MnO₂ (R=0.40, n=54) changes a little bit compared with that of matrices, but the correlation of Co and free Fe-oxide (Fed) (R=0.45, n=54) obviously improved beside that Co and MnO₂ shows high correlation (R=0.71, n=54). There are shown positive correlations of Cu and Zn (R=0.75, n=54), Pb and Co (R=0.38, n=54), Zn and Cd (R=0.46, n=54) in matrices, respectively. There are also shown positive correlations in cutans. These metals all also show positive correlations with MnO₂ in cutans. Therefore, the differentiation degrees of Mn/Fe, and Co/Ni are higher, but those of Cu/Zn, Pb/Co and Zn/Cd molar ratios are low in the process of translocation from matrix soils to cutans, respectively.

Table 6. Correlation coefficient (R) of selected elemental concentrations in cutans and matrix soils.

	MnO ₂		Fed ^a		Co		Pb		Cu		Zn		Ni	
	C ^b	M ^c	C	M	C	M	C	M	C	M	C	M	C	M
MnO ₂	1	1												
Fed	<u>0.46</u> ^d	-0.24	1	1										
Co	<u>0.71</u>	<u>0.72</u>	<u>0.45</u>	<u>-0.45</u>	1	1								
Pb	<u>0.75</u>	<u>0.38</u>	<u>0.58</u>	0.11	<u>0.94</u>	<u>0.38</u>	1	1						
Cu	0.22	<u>-0.35</u>	0.06	<u>0.29</u>	0.22	<u>-0.40</u>	0.20	-0.19	1	1				
Zn	<u>0.34</u>	<u>-0.35</u>	0.02	0.18	0.21	<u>-0.50</u>	0.20	<u>-0.42</u>	0.11	<u>0.75</u>	1	1		
Ni	<u>0.40</u>	<u>0.55</u>	<u>-0.37</u>	<u>-0.42</u>	0.00	<u>0.61</u>	-0.11	<u>0.29</u>	-0.01	-0.03	0.25	-0.04	1	1
Cd	<u>0.66</u>	<u>-0.40</u>	0.20	0.04	<u>0.27</u>	<u>-0.36</u>	<u>0.29</u>	<u>-0.53</u>	0.12	<u>0.27</u>	0.23	<u>0.46</u>	<u>0.49</u>	<u>-0.39</u>

^aFed = Fe soluble in dithionite-carbonate-citrate; ^bC = Cutan; ^cM = Matrix soil; ^dThe underlined datum was a significant statistical correlation at $P < 0.05$ or 0.01 ($n=54$, $r_{0.05}=0.27$, $r_{0.01}=0.35$).

Conclusions

The tested trace elements, especially Ba, Co and Pb, are enriched in the iron-manganese cutans. These trace elements move from matrix soils to cutans with Fe- and Mn-oxides abundantly. Ba, Zn, Cd, Co, Cu, Ni and Pb are mainly enriched in Mn-oxides, but Cr, Li and Mo mostly exist with Fe-oxides. Mn/Fe and Co/Ni molar ratios show higher differentiation degrees than those of Cu/Zn, Pb/Co and Zn/Cd molar ratios in the cutans compared with those in matrix soils. Iron-manganese cutans are possible geochemical information carriers of trace elements translocated in pedons during pedogenesis.

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