NOTE

Enrichment of trace elements in ferromanganese concretions from terra rossa and their potential desorption

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The distributions of trace elements in ferromanganese concretions (FMCs) and the surrounding terra rossa (TR) matrix overlying dolomite have been examined to extend our understanding of their mobilization, redistribution and fractionation during karst weathering and pedogenesis. This study demonstrates that the characteristics of trace elements in TR have been severely overprinted by weathering and pedogenetic processes. The composition of trace elements in FMCs within TR soil profiles varies greatly with depth. The concentrations of Be, Ni, Cu, Zn, As and Bi in FMCs fluctuate and tend to increase with depth; other trace element concentrations fluctuate in the profile but show no clear trend. The toxic elements Cr, As, Cd, Tl and Pb, as well as Co, are significantly enriched in FMCs relative to the surrounding TR matrix: arsenic exhibits strong affinity with Fe, but Cr and Cd contents are not significantly correlated with either Mn or Fe. Correspondingly, Co, Tl and Pb are related to the Mn in FMCs rather than the Fe. In FMCs, trace element distribution and partitioning in the Mn–Fe phases are governed by the location-specific formational pedoenvironment, with the weathering front etching downwards. Experiments with simulated acid rain indicate that desorption of elements from FMCs is generally pH-dependent regardless of the variation of the released amounts and their desorbability. Moreover, it seems that toxic elements bonded to Mn-phase were easily desorbed from FMCs. As a result, the bioavailability, mobility and activity of some toxic elements in FMCs and TR are potentially increased in field areas experiencing severe soil erosion and acid rain.

Keywords: dolomite, karst weathering, terra rossa, ferromanganese concretions, simulated acid rain, toxic element desorption

INTRODUCTION

Ferromanganese concretions (FMCs) occur mainly in soils and in lacustrine and pelagic sediments (McKenzie, 1975; Williams and Owen, 1992; Verlaan *et al.*, 2004; Feng, 2010, 2011). Marine FMCs have been extensively studied because of their economic potential (Calvert and Piper, 1984; Ahmad and Husain, 1987; Glasby *et al.*, 1987). In spite of having little economic potential, FMCs in soils possibly play an important role for the pedobiosphere. Mn and Fe are important elements for plant and animal nutrition (Liu *et al.*, 2002). In addition, oxides and/or hydroxides of both Mn and Fe are the main Mn–Fe phases in the soils, and they often act as strong scavengers of trace elements during weathering and pedogenesis (Burns, 1976; McKenzie, 1980; Bellanca *et*

al., 1996; Palumbo *et al.*, 2001; Cornu *et al.*, 2005; Feng, 2011). Therefore, knowledge of the distribution of trace elements in FMCs is valuable in geochemical exploration since it provides a valid procedure for selection of sample medium and extraction, and helps evaluate the significance of analytical data (Chao and Theobald, 1976; Miko *et al.*, 1999). On the other hand, Mn and Fe also affect the mobility of trace elements in soils and the phytoavailability of both nutrient and toxic trace elements (Bellanca *et al.*, 1996; Palumbo *et al.*, 2000, 2001; Liu *et al.*, 2002). Through mechanisms such as co-precipitation, adsorption and lattice substitution, among others, the trace elements are scavenged from the soil solution, and are incorporated into FMCs (Chao and Theobald, 1976); however, once the pedoenvironment has been changed, the trace elements adsorbed in FMCs become chemically unstable, possibly desorbing into the soil solution (Taylor and McKenzie, 1966; Bellanca *et al.*, 1996).

Although trace elements in FMCs from many soils have been studied (Taylor and McKenzie, 1966; Dawson

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Fig. 1. (A) Simplified stratigraphic section of TR profile at the Dashandong site; (B) variation of pH (KCl) value in TR matrix with depth; (C) variation of mean grain size in TR matrix with depth; (D) variation of quartz content in TR matrix with depth; (E) variation of SiO₂ content in TR matrix with depth (after Feng *et al.*, 2009a).

et al., 1985; Latrille *et al.*, 2001; Liu *et al.*, 2002; Cornu *et al.*, 2005), few have focused on the distribution of trace elements in FMCs at different depths in the soil profile (Feng, 2010, 2011). There is also a lack of information both on the direct quantitative relationship between Mn-Fe phases and trace elements, and on the comparative capacities of the Mn- and Fe-phases to retain trace elements in FMCs at different depths and in various pedoenvironments (Chao and Theobald, 1976).

The origin of terra rossa (TR) and its relationship with the underlying carbonate rocks poses long-standing and controversial questions (Yaalon, 1997; Durn *et al.*, 1999; Wang *et al.*, 1999; Durn, 2003; Ji *et al.*, 2004; Singer, 2007; Merino and Banerjee, 2008; Feng *et al.*, 2009a, b; Muhs and Budahn, 2009; Muhs *et al.*, 2010). Some TR is not the product of weathering *in situ*, and therefore does not have a close genetic relationship with the carbonate rocks underlying it, and probably does not provide the best opportunity for uncovering the behavior of trace elements during karst weathering (Feng *et al.*, 2009a, b); however, trace elements have been used to determine TR origin (Whitehead *et al.*, 1993; Ji *et al.*, 2004; Mee *et al.*, 2004; Muhs and Budahn, 2009; Muhs *et al.*, 2010). Whatever the case may be, a sound knowledge of the geochemical behavior of trace elements during karst weathering and pedogenesis is required for logically trac-

ing the TR origin (Feng, 2011).

The present study investigated a 5.4 m thick *in situ* terra rossa weathering profile overlying dolomite. FMCs occur in the TR (Feng *et al.*, 2009a). The main objectives of the study were to investigate (1) the trace element composition in the FMCs and TR matrix, and their distribution in the profile; (2) the enrichment behavior of trace elements in the FMCs compared to the surrounding TR matrix; (3) specific inter-element associations between Mn and Fe and the trace elements in the FMCs; and (4) the potential desorption of trace elements from the FMCs and TR due to human activity.

GEOLOGICAL SETTING AND DATA ON THE TR PROFILE

The Dashandong terra rossa profile lies 4 km north-west of Guiyang city, on the Yunnan-Guizhou Plateau in south-western China. The sampling site lies at the pediment of a karst hill with TR up to 5.4 m thick overlying Early Triassic dolomite (Feng *et al.*, 2009a).

Field observations showed that the TR profile is heterogeneous in both color and texture, and comprises two horizons (Fig. 1). Horizon I (0–2.5 m) is silty clay and clay: light-brownish-grey soil and anthropogenic slag deposits (0–0.1 m), silty clay, mainly reddish-yellow (0.1–1.2 m), and reddish-yellow clay (1.2–2.5 m) that exhibits

enhanced plasticity and has a massive and compact structure. A few FMCs (generally 1–4 mm in diameter) are scattered below 0.4 m, with brown pisolitic or crustose surfaces (sample DSD-39FMC, dry powder, Munsell color 7.5YR 4/4; others colored 10YR 4/3). Enrichment of some crustose FMCs occurs at approximately 1.7 m depth, with a maximum concretion size of $3 \times 2.5 \times 1$ cm (sample DSD-38FMC). The largest pisolitic concretion, 8 mm in diameter, was found at 2.0 m depth (sample DSD-35FMC); its internal structure displayed a discontinuous succession of concentric bandings based on back-scattered electron (BSE) imaging observations (Feng *et al.*, 2003). Its boundary with the underlying horizon was gradual and irregular.

Horizon II (2.5–5.4 m) consists of mottled clay with common reddish-yellow to light-grey spots. The TR exhibits a clayey texture, a massive and blocky structure, and a complete lack of visible bedding features or clear transitions. A few flake-like, reddish-brown FMCs (dry powder, Munsell color 2.5YR 4/4 for samples DSD-30FMC, DSD-22FMC, DSD-17FMC and DSD-11FMC) and fine pisolitic FMCs (generally <1 mm in diameter), brown in color (dry powder, Munsell color 10YR 4/3 for sample DSD-14FMC) were found at depths of 2.5 to 4.4 m. Additionally, a few strongly weathered dolomite relics were included in the TR matrix between 5.0 and 5.4 m depth (Fig. 1A). The contact between the TR and the underlying dolomite was sharp and irregular.

The dolomite bedrock occurs at a depth of 5.4 m, being strongly weathered from 5.4 to 5.45 m. The weathered dolomite crumbles easily to dolomitic sand. Below 5.45 m, weakly weathered dolomite gradually transits into hard dolomite.

Disturbed bulk samples of TR collected at 0.1 m intervals in the fresh profile were used for FMC collection and for major and trace element analyses. FMCs were handpicked from the bulk TR samples and cleaned ultrasonically in super-pure water.

The fresh dolomite contained 0.69% insoluble residue (IR) on average following acid treatment, consisting of illite, illite/smectite mixed-layer minerals, quartz, hematite, pyrite, and small amounts of feldspar (Feng *et al.*, 2009a).

X-ray diffraction (XRD) powder analysis showed that the brown FMCs contained gibbsite, quartz and small amounts of illite and kaolinite (Feng *et al.*, 2011), suggesting goethite as the principal crystalline component of the Fe phase. By contrast, the sheet-like, reddish-brown FMCs comprised quartz, hematite, illite and kaolinite; analysis suggested that hematite was the principal crystalline component of the Fe phase in these concretions. However, XRD analysis of the FMC samples did not reveal distinct peaks for Mn-oxide minerals, probably due to the poorly crystallized Mn mineral phase.

Feng *et al.* (2009a) suggested that the TR in the Dashandong profile is probably an *in situ* weathering crust, based on content, grain size distribution, morphology and $\delta^{18}\text{O}$ of the contained quartz; however, the parent rocks are vertically heterogeneous. The TR partly consists of the insoluble residue of the underlying dolomite, enriched by elements imported by percolating external soil-water and/or from pre-existing TR at the top of the profile.

METHODS

Insoluble residue (IR) in the dolomite was isolated by: (1) treating with 0.3M acetic acid (HOAc) at room temperature, retaining some undissolved dolomite at all times to help prevent alteration of the characteristics of the clays (Ostrom, 1961); then (2) dissolving the residual dolomite using a pH 4.5 HOAc/NaOAc buffer (Rabenhorst and Wilding, 1984).

Powder samples of the TR matrix (excluding possible FMCs), FMCs, dolomite, and IR from the underlying dolomite were dissolved using the pressurized acid-digestion procedures described by Qi *et al.* (2000). The concentration of trace elements in all samples, and the Mn and Fe content in the TR matrix (excluding possible FMCs), the dolomite and the IR from the underlying dolomite were all measured on an inductively coupled plasma mass spectrometer (ICP-MS; X-7 series) at the Institute of Tibetan Plateau Research (ITP), Chinese Academy of Sciences (CAS). For quality control, the USGS reference material AGV-2 (andesite) was analyzed. The difference between our laboratory data and the recommended and information values for AGV-2 was <5% for Li, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Rb, Sr, Zr, Ba, Ta, Tl, Pb, Th and U, and <10% for Be, Zn, Ga, Nb, Cs and Hf. (No recommended and information values are available for B, As, Cd, Sn or Bi in conjunction with the reference material AGV-2. See Appendix Table A1 available at <http://www.terrapub.co.jp/journals/GJ/archives.html>.) The Mn and Fe content in the FMCs was measured using the inductively coupled plasma optical emissions spectrometer (ICP-OES; Prodigy, Teledyne Leeman Labs) at ITP, CAS.

The effect of pH change on the processes of trace element desorption from FMCs was determined using the simulated acid rain method. Based on the chemical composition of the rainfall in southern China, the simulated acid rains in this experiment were 4:1 H_2SO_4 : HNO_3 mole ratio at pH values 2.1, 3.0, 4.0 and 5.4 (Wang *et al.*, 2009). A solution of each of these was added to test tubes containing 0.5 g samples of FMCs (sample DSD-38FMC) at a sample:solution ratio of 1:20. The suspensions were shaken for 2 h in a horizontal reciprocating shaker (120 rpm, 26°C). After further equilibration for 22 h at room temperature, the suspensions were centrifuged and the

Fig. 2. Concentration of trace elements in FMCs, TR matrix, dolomite (Dol.) and IR from the underlying dolomite varies with depth in the Dashandong profile. Element concentration of the upper continental crust (UCC); data after Taylor and McLennan (1985) shown for comparison.

Fig. 2. (continued).

residual FMCs then rinsed twice with Milli-Q™ water (resistivity 18.2 MΩ·cm). The leachates were filtered on 0.45 μm syringe filters in preparation for measuring the concentrations of released elements using the ICP-MS at ITP. Meanwhile, blank determinations with solutions at various pH had been completed. The released amounts of elements from the FMCs were calculated on the basis of untreated sample weight. The desorbability of the elements in the FMCs (amount desorbed expressed as a percentage of the total) was calculated from their concentrations in the bulk FMCs.

RESULTS AND DISCUSSION

Figure 2 shows the trace element concentration in the FMCs, the surrounding TR matrix, the dolomite and the IR from the underlying dolomite, at different depth (Appendix Table A2 including these data is available at <http://www.terrapub.co.jp/journals/GJ/archives.html>). Although Ti, Mn and Fe are considered major elements, they are included here as well for comparison with the trace elements (see Appendix Table A2 available at <http://www.terrapub.co.jp/journals/GJ/archives.html>).

Comparison of trace element distribution in TR and IR

Compared to the IR from the underlying dolomite, the TR matrix is enriched in Li, Be, Sc, Mn, Co, Ni, Zn, Rb, Cd, Cs, Tl and Th (Fig. 2); in contrast, B, V, Cr, Fe, Cu, Ga, As, Pb, Bi and U are depleted. The concentrations of Ti, Zr, Nb, Hf and Ta in the IR are similar to that deeper in the profile, but are less than in the upper profile. Additionally, Sr, Sn and Ba have similar distributions in both the IR and the TR matrix. Marques *et al.* (2004) reported that, for trace elements over long periods of pedogenic weathering at acid pH, mono- and divalent cations were leached and depleted, while tri-, tetra- and pentavalent elements accumulated. In the present study, it is not clear that the depletion and enrichment of the trace elements in the TR depended on their valence during weathering. The present results support the previous conclusions of Feng (2011).

Distribution of trace elements in TR and FMCs with depth

In the TR matrix, the concentrations of Be, B, V, Fe, Cu, Zn, Ga, As, Cd, Tl, Pb and U tend to increase with depth (Fig. 2). Such a pattern indicates that these elements are removed from the upper and middle sections of the TR profile, transferred downwards, then precipitated at the deepest part of the profile. The concentrations of the high field strength (HFS) elements Ti, Zr, Nb, Hf and Ta tend to decrease with depth from 0 to 2.3 m; in contrast, their concentrations exhibit little variation in the deepest part of the profile (2.3–5.4 m). HSF elements are commonly conservative; therefore, their variation in the pro-

file indicates that the profile itself is heterogeneous, and also shows the imprint of detritic minerals in the parent rocks. In fact, these results accord with field observations and our previous findings based on quartz features in TR (Feng *et al.*, 2009a).

The concentrations of Li, Sc, Ni, Rb and Cs in the TR matrix show an increasing trend in the upper-to-middle depth range, but a decreasing tendency in the deepest part of the profile. Several trace elements, including Sr, Ba, Bi and Th, show little variation in the profile; Sn also exhibits little variation except for two strong peaks within the profile. The concentrations of Cr and Mn fluctuate with no clear tendency across the profile, whereas Co concentration tends to decrease with depth.

Generally, the trace element concentrations in FMCs showed complex fluctuating variation with depth (Fig. 2). The concentrations of Be, Ni, Cu, Zn, As and Bi fluctuate, but tend to increase with depth; the others fluctuate with no clearly discernable trend. These fluctuating distributions of trace elements with depth in FMCs are similar to those reported by Feng (2011) for another TR profile.

Moreover, Feng (2011) found that Be exhibited a similar geochemical behavior as that of rare earth elements (REEs; except for Ce) and Y in FMCs and TR matrix for another TR profile. Feng (2011) explained that Be may be mobilized and transferred as soluble Be-organic complexes similarly to REEs, and their mobility is highly dependent on pH. In the present work, Be also demonstrated a strong geochemical relationship with REEs (except for Ce) in the FMCs and the TR matrix (e.g., $r_{\text{Be-La}} = 0.83$, $r_{\text{Be-Lu}} = 0.97$, $P < 0.001$ in TR; $r_{\text{Be-La}} = 0.90$, $r_{\text{Be-Lu}} = 0.91$, $P < 0.001$ in FMCs. see Feng *et al.*, 2011 for REE data); but Y only in the TR exhibited significant correlation with Be ($r_{\text{Be-Y}} = 0.92$, $P < 0.001$ in TR; $r_{\text{Be-Y}} = 0.44$, $P = 0.1$ in FMCs). Therefore, a similar geochemical behavior between Be and REEs (except for Ce) seems to be a general phenomenon during karst weathering and TR formation.

Enrichment of trace elements in FMCs

To understand trace element enrichment in FMCs with respect to the surrounding TR matrix, the element enrichment factor (EF) for the FMCs was determined from the relationship suggested by Rankin and Childs (1976):

$$EF = \frac{\text{element concentration in FMC}}{\text{element concentration in surrounding TR matrix}}.$$

The results are represented in Fig. 3.

Compared to the TR matrix, FMCs were enriched with Cr, Mn, Fe, Co, As, Cd, Tl and Pb. In contrast, Li, Ti, Ga, Rb, Sr, Zr, Nb, Sn, Cs, Hf, Ta and Th show little deple-

Fig. 3. Distribution pattern of element enrichment factors ($EF = \text{element concentration in FMCs} / \text{element concentration in surrounding TR matrix}$) for FMCs. Vertical bars represent the spread of data (min and max).

tion in the FMCs relative to the TR matrix. The EF s for Be, B, Sc, V, Ni, Cu, Zn, Ba, Bi and U all approach 1, indicating no discernible enrichment or depletion compared to the matrix. Additionally, none of the trace element EF values fluctuate across the profile with any clear tendency.

During weathering front downward-etching of the local base level, the specific pedoenvironment—such as existing redox condition (Eh and pH), reactivity and degree of crystallinity of the Mn–Fe phases, together with their relative abundance with depth in the TR profile—has varied due to tectonic activity and/or climate change (Chao and Theobald, 1976; Bellanca *et al.*, 1996). This change in specific pedoenvironment may directly influence the distribution of trace elements in FMCs with depth.

Trace element partitioning with Mn–Fe phases in FMCs

In the Dashandong terra rossa profile, it is worth noting that the toxic elements Cr, As, Cd, Tl and Pb, as well as Co, were significantly enriched in the FMCs compared to the surrounding TR matrix (Fig. 3). Cobalt shows a strong affinity for the Mn phase in the FMCs ($r_{\text{Mn-Co}} = 0.80$, $P < 0.001$; $r_{\text{Fe-Co}} = -0.65$, $P < 0.01$). Associations between toxic elements and Mn–Fe phases in the FMCs are set out below.

Chromium Cr is frequently co-associated with Fe in natural lateritic Fe-oxide crusts and ferromanganese nodules (Singh and Gilkes, 1992; Schwertmann and Pfab, 1994; Liu *et al.*, 2002; Marques *et al.*, 2004). The data in the present work indicates that the close co-associations of Cr with Mn and Fe are not specific to the formation of FMCs ($r_{\text{Mn-Cr}} = -0.04$, $P = 0.89$; $r_{\text{Fe-Cr}} = 0.01$; $P = 0.975$). This is consistent with other results from Fe-oxide crusts (ferricretes) in laterite reported by Marques *et al.* (2004).

Arsenic The enrichment of As in FMCs has been observed

and discussed earlier by Rankin and Childs (1976, 1987). Rankin and Childs (1976) suggested that As was associated with an Fe-phase in FMCs. Compared with the TR matrix, FMCs and IR from the underlying dolomite contained much more As. Arsenic enrichment in IR results from the presence of pyrite, since pyrite is generally arsenic-rich (Price and Pichler, 2006). The FMCs had an As concentration between 65.2 and 781.2 ppm (average 313.4 ppm, $n = 15$). For the Dashandong profile, statistical analysis suggests that this is related to the degree of Fe enrichment rather than Mn enrichment ($r_{\text{Mn-As}} = -0.66$, $P < 0.01$; $r_{\text{Fe-As}} = 0.84$, $P < 0.001$).

Cadmium Palumbo *et al.* (2001) reported that Cd was related to Mn rather than Fe enrichment in the ferromanganese nodules of TR. Liu *et al.* (2002) also observed this behavior in ferromanganese nodules from a Chinese alfisol. In the investigated TR profile, Cd does not exhibit significant correlation with either Mn or Fe in the FMCs ($r_{\text{Mn-Cd}} = 0.19$, $P = 0.50$; $r_{\text{Fe-Cd}} = 0.23$, $P = 0.42$).

Thallium Bidoglio *et al.* (1993) and Koschinsky and Halbach (1995) suggested that surface precipitation of Ti_2O_3 on $\delta\text{-MnO}_2$ as a result of Tl(I) sorption, and that oxidation at the mineral surface could explain the strong Tl enrichment in the ferromanganese crusts. In the Dashandong profile, Tl has a significant affinity for the Mn-phase in FMCs ($r_{\text{Mn-Tl}} = 0.74$, $P < 0.001$; $r_{\text{Fe-Tl}} = -0.35$, $P = 0.21$).

Lead Childs (1975) and Rankin and Childs (1987) pointed to higher concentrations of Pb in FMCs than in the corresponding surrounding soil materials. Cornu *et al.* (2005) found that accumulation of Pb in the ferromanganese nodules was due to the high specific adsorption of Pb by the Mn oxides. In contrast, Palumbo *et al.* (2001) reported that Pb appeared to be associated with the Fe-rich phase

Fig. 4. TR erosion and stone tooth outcropping in karst region on the Yunnan–Guizhou Plateau.

in ferromanganese nodules. The data in the present work indicates that Pb exhibits a significant affinity for the Mn-phase in FMCs ($r_{\text{Mn-Pb}} = 0.79$, $P < 0.001$; $r_{\text{Fe-Pb}} = -0.36$, $P = 0.18$).

In summary, the present work shows that, in the FMCs, arsenic exhibits significant affinity for Fe; Cr and Cd have no significant correlation with either Mn or Fe; and Co, Tl and Pb are related to Mn rather than Fe.

Feng (2011) reported that FMCs in the Pingba Farm TR profile were significantly enriched in Mn, Co, Cd, Tl and Pb compared to the TR matrix. Correspondingly, the Fe in FMCs did not show discernible enrichment or depletion. Moreover, only Co appeared to be associated with Mn-rich phases in FMCs, whereas Cd, Tl and Pb showed significant affinity for Fe-phases in FMCs. Comparing these findings with the present work implies that the enrichment of Mn, Co, Cd, Tl and Pb in the FMCs from the TR profile seems to be a common phenomenon. Corresponding to this, the distributions of Cr, As and even Fe in the FMCs may vary between TR profiles. It is noteworthy that a close relationship between Co and Mn was found in all the FMCs examined in the TR profiles, which suggests a specific scavenging effect of the Mn for Co (Taylor and McKenzie, 1966). The toxic elements Cd, Tl and Pb, however, showed different associations within the Mn–Fe phases, further suggesting that the scavenging activity of the Mn–Fe phases changes under different pedoenvironments, and may be extremely complex. As the trace element distributions in the FMCs vary with depth, the trace element partitioning in the Mn–Fe phases is also governed by the specific pedoenvironment of different TR soil profiles (Feng, 2010, 2011).

Potential desorption of trace elements from FMCs

The present research area is located in the central region of a karst area in south-western China where FMCs are widespread in TR soils and are rich in trace elements (Wang *et al.*, 2001; Feng *et al.*, 2003; Su *et al.*, 2008; Feng, 2010, 2011). However, soil erosion has become a serious environmental problem in the region (Fig. 4; Yuan, 1997; Wang *et al.*, 2004; Huang and Cai, 2007). Aside from the risk of surface soil loss, significant soil erosion potentially involves extensive exposure of the terra rossa base, and especially the FMCs contained in it. Unfortunately, the research region also suffers the most pressing acid rain problem in China (Zhao *et al.*, 1988; Larssen and Carmichael, 2000; Larssen *et al.*, 2000; Hao *et al.*, 2001; Meng *et al.*, 2002). Additionally, TR, especially when it is intensively weathered, has a weak buffering capacity for acid rain, to which it is also vulnerable and sensitive (Tao *et al.*, 2002); thus, acid rain can potentially lead from one disaster to another.

The results of the simulated acid rain experiments are shown in Figs. 5 and 6. These indicate that desorption of toxic trace elements (except arsenic) from FMCs is pH-dependent; in general, both the released amounts and desorbability of toxic trace elements from FMCs correlate well with increasing acidity of the simulated acid rain. Different desorption properties of the trace elements in the FMCs were also observed: Co, Cd and Tl were more easily desorbed than either Cr or Pb (Fig. 6). No arsenic was detected. Such differences in quantity and desorbability are perhaps caused by the different affinities of the bonding sites to the toxic elements.

Experimental results demonstrate that desorption of

Fig. 5. Amounts of elements released from FMCs treated with simulated acid rain solutions at varied pH.

Fig. 6. Desorbability of elements from FMCs as a function of solution pH.

Mn, Fe and Ce from FMCs is also pH-dependent (Figs. 5 and 6). In contrast to Fe, Mn exhibited higher released amounts (Fig. 5), meanwhile Mn and Ce were more easily desorbed from FMCs (Fig. 6). Feng *et al.* (2011) reported that the enrichment of Ce in FMCs was correlated with Mn in the Dashandong TR profile. In addition, a specific scavenging effect of Mn for Co has been described above. These lines of evidence support that trace elements desorbed from FMCs seem to be mainly derived from those bonded to Mn-phase. As a result, the bioavailability, mobility, and activity of toxic elements in terra rossa soil are all possibly greatly increased by acid rain.

CONCLUSIONS

Based on our measurements and the discussion above, it was found that:

(1) The concentrations of most trace elements in the terra rossa (TR) in the Dashandong profile did not fall within the range defined by the insoluble residue (IR) from the underlying dolomite. Although it is produced by *in situ* weathering, the trace element distribution in the TR is not simply inherited from the underlying dolomite. Correspondingly, the characteristics of the trace elements in the TR were significantly overprinted by mobilization, redistribution and fractionation during karst weathering and pedogenesis.

(2) The present work revealed that ferromanganese concretions (FMCs) in the TR matrix contained highly variable trace element compositions at different depths. The concentrations of Be, Ni, Cu, Zn, As and Bi in FMCs fluctuated, tending to increase with depth; the others fluctuated but with no clear trend in the profile. Compared to the TR matrix material, the concretions were found to be

enriched in Cr, Mn, Fe, Co, As, Cd, Tl and Pb; however, they contained a little less Li, Ti, Ga, Rb, Sr, Zr, Nb, Sn, Cs, Hf, Ta and Th than the TR matrix, and they showed neither enrichment nor depletion of Be, B, Sc, V, Ni, Cu, Zn, Ba, Bi or U. In addition, no clear tendency was observed for the trace element fractionation between FMCs and the corresponding TR matrix. The fluctuation of trace element abundance in FMCs with depth may reflect the specific pedoenvironmental history during FMC formation, with the weathering front etching downwards.

(3) The concentration of the toxic elements Cr, As, Cd, Tl and Pb in the FMCs appeared to be abnormally high. Arsenic typically exhibited a significant affinity for Fe. Neither Cr nor Cd showed any significant correlation with either Mn or Fe, but both Tl and Pb showed a preferred association with Mn rather than Fe. A comparative study revealed that toxic element partitioning in the FMC Mn-Fe phases is specific to the pedoenvironment that prevailed during the formation of individual TR soil profiles.

(4) Simulated acid rain experiments indicated that desorption of elements from FMCs is generally pH-dependent regardless of any other variation in their released quantities and desorbabilities. Moreover, it seems that toxic elements bonded to Mn-phase were easily desorbed from FMCs. As a result, the bioavailability, mobility, and activity of toxic elements from FMCs and TR are potentially increased in field situations where major soil erosion occurs in conjunction with acid rain.

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