

# Improved methods for selective dissolution of Mn oxides: applications for studying trace element associations

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## Abstract

The association of rare earth and other trace elements with Fe and Mn oxides was studied in Fe-Mn-nodules from a lateritic soil from Serra do Navio (Northern Brazil). Two improved methods of selective dissolution by hydroxylamine hydrochloride and acidified hydrogen peroxide along with a classical Na-citrate-bicarbonate-dithionite method were used. The two former reagents were used to dissolve Mn oxides without significant dissolution of Fe oxides, and the latter reagent was used to dissolve both Mn and Fe oxides. Soil nodules and matrix were separated by hand. Inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry after fusion with lithium metaborate, and X-ray diffraction were used to determine the elemental and mineralogical composition of the nodules and soil matrix. The latter was composed of kaolinite, gibbsite, goethite, hematite, and quartz. In the nodules, lithiophorite  $\text{LiAl}_2(\text{Mn}_2^{\text{IV}}\text{Mn}^{\text{III}})\text{O}_6(\text{OH})_6$  was detected in addition to the above-mentioned minerals. The presence of hollandite ( $\text{BaMn}_8\text{O}_{16}$ ) and/or coronadite ( $\text{PbMn}_8\text{O}_{16}$ ) in the nodules is also possible. In comparison to the matrix, the nodules were enriched in Mn, Fe, K, and P, and relatively poor in Si, Al, and Ti. The nodules were also enriched in all trace elements determined. Phosphorus, As and Cr were associated mainly with Fe oxides; Cu, Ni, and V were associated with both Fe and Mn oxides; and Ba, Co, and Pb were associated mainly with Mn oxides. Distribution of rare earth elements indicated a strong positive Ce-anomaly in the nodules, compared to the absence of any anomaly in the matrix. Some of Ce was associated with Mn oxides. The improved methods achieved almost complete release of Mn from the sample without decreasing the selectivity of dissolution, i.e., without dissolving significant amounts of Fe oxides and other minerals, and provided reliable information on associations of trace elements with Mn oxides. These methods are thus proposed to be included in sequential extraction schemes for fractionation of trace elements in soils and sediments.

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## 1. Introduction

It is well known that the mobility and bioavailability of trace elements, as well as their ecological toxicity,

depends strongly on their chemical forms and ways of binding rather than on the total element contents (e.g., McBride, 1994). Determination of specific chemical species or binding forms, however, is difficult and often hardly possible. In practice, single selective dissolution methods and sequential extraction schemes have been developed for determination of broader binding forms of trace elements in soils and sediments. Such techniques have been used increasingly by environmental chemists, soil scientists and geologists (e.g., Rauret et al., 1999).

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Manganese oxides are known to have a high sorption capacity for many trace elements, including oxyanions (e.g., molybdate, phosphate, selenite, arsenate) and hydrolyzed cations (e.g.,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ). These elements can be strongly adsorbed on oxide surfaces, even in the presence of a large excess of indifferent electrolyte (see, e.g., references in McKenzie, 1989). Thus, Mn oxides may control the mobility of trace elements in the environment and their availability to plants.

The dissolution and precipitation of Mn and Fe (as well as trace elements associated with them) in soils are affected by changes in the redox potential. Manganese reduction is classically considered to occur at Eh values higher than those of Fe. Manganese may be mobilized even in slightly reducing environments, before Fe is reduced (Gotoh and Patrick, 1972; Gotoh and Yamashita, 1967; McBride, 1994). Thus, analytical separation of Mn and Fe oxides is necessary to gain sound information as both of these phases can host trace elements but differ considerably in their mobility under reductive conditions.

Taylor and McKenzie (1966) used 10%  $\text{H}_2\text{O}_2$  in 0.001 M  $\text{HNO}_3$  to extract Mn oxides, but reported that <50% of the total Mn in the samples was removed after 3 days of treatment. Chao (1972) used 0.1 M  $\text{NH}_2\text{OH-HCl}$  in 0.001 M  $\text{HNO}_3$  (pH 2) for selective dissolution of Mn oxides. The average dissolution of Mn oxides was 85% in various sediments, but only 50% in soils.

Literature suggests that the method of Taylor and McKenzie (1966) has not been used extensively, except perhaps in the study of Ross et al. (1976). The method of Chao (1972), on the other hand, has been used widely. For example, it was included in the well-established fractionation scheme of Shuman (1985), used by Tokashiki et al. (1986), Belzile et al. (1989), Benitez and Dubois (1999), La Force and Fendorf (2000), and Quantin et al. (2002).

Incomplete release of Mn by selective dissolution methods proposed in the past definitely severely limits the discussion on the associations of trace elements with Mn oxides. Recently, Neaman et al. (2004) used an approach of determining the stoichiometry of the reactions for improvement of the methods reported in the literature. The authors showed that incomplete dissolution of Mn oxides reported by Taylor and McKenzie (1966) is due to the lack of added acid and that reported by Chao (1972) is due to the lack of added hydroxylamine hydrochloride. These two methods were improved by increasing the amount of solution for a given amount of solid in the case of  $\text{NH}_2\text{OH-HCl}$  treatment and by increasing acid concentration in the case of  $\text{H}_2\text{O}_2$  treatment.

The present paper is intended to demonstrate the ability of the above-mentioned improved methods for determining the associations of rare earth and other

trace elements with Mn oxides. The authors have chosen Fe–Mn-nodules from a lateritic soil as an object of the present study since such nodules are known to contain elevated Mn concentrations and to be enriched in many trace elements (e.g. McKenzie, 1989; Dixon and Skinner, 1992).

## 2. Materials and methods

Lateritic subsoil (depth 0.75 m) from Serra do Navio (Northern Brazil) was selected for the study. Detailed description of the site studied is given elsewhere (Mou  l  , 2003; profile No. SN26). The soil contained nodules of 2–5 mm in diameter. The nodules were removed from the soil by hand. Remaining soil was as free of nodules as possible and was referred to hereafter as “matrix”. Both the matrix and the nodules were finely ground in an agate mortar.

X-ray diffraction (XRD) data were obtained using a Philips diffractometer with  $\text{Co } K_\alpha$  radiation. For chemical analyses, the samples were decomposed by fusion with  $\text{LiBO}_2$  and dissolved in  $\text{HNO}_3$ . Major element contents were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Jobin-Yvon JY 70), trace element contents (including rare earth elements (REE7) were determined by inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer 5000). Calibration curves were plotted using at least 8 international geostandards (Govindaraju, 1994) that were decomposed as samples (with  $\text{LiBO}_2$  and dissolved in  $\text{HNO}_3$ ). For quality control purposes, some international geostandards (other than those for calibration) were used following the same decomposition procedure as samples.

The nodules were used for further experiments of selective dissolution. Three reagents were used: (1) hydroxylamine hydrochloride, (2) acidified hydrogen peroxide, and (3) Na-citrate-bicarbonate-dithionite (referred hereafter to as “ $\text{NH}_2\text{OH-HCl}$ ”, “ $\text{H}_2\text{O}_2$ ” and “CBD”, respectively). Procedures (1) and (2) have been discussed in detail in Neaman et al. (2004). Procedure (3) is based on that proposed by Mehra and Jackson (1960). The procedures were as follows:

- (1) 0.1 M  $\text{NH}_2\text{OH-HCl}$ , non-acidified (pH = 3.6), solid/solution weight/volume ratio of 1:2000 g/ml (100 mg/200 ml), 2 h stirring at room temperature;
- (2) 50 ml of 30%  $\text{H}_2\text{O}_2$  mixed with 50 ml of 1 M  $\text{HNO}_3$ , solid/solution weight/volume ratio of 1:1000 g/ml (100 mg/100 ml), 30 min stirring at room temperature. A control experiment (0.5 M  $\text{HNO}_3$  without  $\text{H}_2\text{O}_2$ ) with the same solid/solution ratio and the same duration was also carried out;

- (3) 40 ml of 0.3 M sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ), 5 ml of 1 M sodium bicarbonate ( $\text{NaHCO}_3$ ), 1 g of sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ), 1 h stirring at 80 °C (in a water bath), sample weight of 100 mg.

Procedures (1) and (2) were expected to completely dissolve Mn oxides without significant dissolution of Fe oxides. The control experiment was aimed at determining the effect of  $\text{HNO}_3$  added. Procedure (3) was expected to completely dissolve both Mn and Fe oxides.

At the predetermined period of time, the suspensions were filtered using 0.2  $\mu\text{m}$  filters using a vacuum filtering system. Resulting solutions were transferred to volumetric flasks. The solids on the filters were washed 3 times with distilled water that was added to flasks. In the case of the CBD treatment, the suspension was cooled in air prior to filtering. In the case of dissolution by  $\text{H}_2\text{O}_2$ , the solution was heated up to boiling to decompose the reagent, and cooled prior to transferring to a volumetric flask. Then, concentrations of some major and trace elements in the solutions were determined by ICP-AES, those of the REE (in the case of dissolution by  $\text{H}_2\text{O}_2$ ) were determined by ICP-MS. Unfortunately, it was not possible to determine REE by ICP-MS in the case of

dissolution by  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and CBD due to matrix interferences nor by ICP-AES due to very low concentrations of REE. Selective dissolution experiments were performed in duplicates. The deviations in the values obtained from the duplicate runs were  $\leq 10\%$ . The average values are shown here (Table 4).

### 3. Results

According to XRD analyses, the matrix was composed of kaolinite, gibbsite, goethite, hematite, and quartz. In the nodules, lithiophorite  $\text{LiAl}_2(\text{Mn}_2^{\text{IV}}\text{Mn}^{\text{III}})\text{O}_6(\text{OH})_6$  (formula after Post and Appleman, 1994) was detected in addition to the above-mentioned minerals by the presence of X-ray diffraction peaks at 9.49 and 4.74 Å. As discussed below, it is possible that hollandite ( $\text{BaMn}_8\text{O}_{16}$ ) and/or coronadite ( $\text{PbMn}_8\text{O}_{16}$ ) are present in the nodules.

Contents of major, trace, and rare earth elements in the samples are shown in Tables 1–3, respectively. The enrichment factor (EF) for each element was calculated as a ratio of element content in the nodules to that in the matrix. In comparison to the matrix, the nodules were enriched in Mn, Fe, K and P, and depleted in Si, Al and

Table 1  
Major element contents (%) in the nodules and matrix

| Sample  | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MnO   | MgO  | CaO   | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | LOI*  | Total |
|---------|------------------|--------------------------------|--------------------------------|-------|------|-------|-------------------|------------------|------------------|-------------------------------|-------|-------|
| Nodules | 14.67            | 12.55                          | 41.88                          | 13.00 | 0.22 | <0.01 | <0.01             | 0.32             | 1.11             | 0.32                          | 13.72 | 97.79 |
| Matrix  | 31.94            | 27.98                          | 18.36                          | 0.91  | 0.20 | <0.01 | <0.01             | 0.17             | 2.59             | 0.14                          | 16.62 | 98.91 |
| EF**    | 0.46             | 0.45                           | 2.28                           | 14.29 | 1.10 | –     | –                 | 1.88             | 0.43             | 2.29                          | –     | –     |

\* LOI = loss on ignition.

\*\* EF = enrichment factor (calculated as ratio of element content in the nodules to that in the matrix).

Table 2  
Trace element contents (ppm) in the nodules and matrix

| Sample  | As   | Ba   | Cd  | Co   | Cr   | Cu   | Mo   | Ni   | Pb   | Sb   | V   | Zn  |
|---------|------|------|-----|------|------|------|------|------|------|------|-----|-----|
| Nodules | 1252 | 2435 | 2.8 | 216  | 2771 | 333  | 130  | 419  | 357  | 39.9 | 575 | 273 |
| Matrix  | 288  | 176  | 0.3 | 24.3 | 296  | 57.5 | 22.6 | 60.6 | 32.9 | 9.8  | 383 | 103 |
| EF*     | 4.3  | 13.8 | 9.3 | 8.9  | 9.4  | 5.8  | 5.8  | 6.9  | 10.9 | 4.1  | 1.5 | 2.7 |

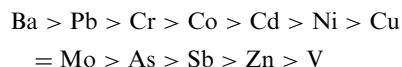
\* EF = enrichment factor (calculated as ratio of element content in the nodules to that in the matrix).

Table 3  
Rare earth element contents (ppm) in the nodules and matrix

| Sample  | La   | Ce   | Pr  | Nd   | Sm  | Eu  | Gd  | Tb  | Dy  | Ho  | Er  | Tm  | Yb  | Lu  |
|---------|------|------|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Nodules | 18.0 | 1077 | 4.7 | 17.8 | 4.1 | 1.1 | 6.9 | 0.7 | 4.2 | 0.8 | 2.4 | 0.4 | 2.7 | 0.4 |
| Matrix  | 26.5 | 52.5 | 4.5 | 14.6 | 2.4 | 0.5 | 2.0 | 0.4 | 2.2 | 0.5 | 1.4 | 0.2 | 1.6 | 0.3 |
| EF*     | 0.7  | 20.5 | 1.0 | 1.2  | 1.7 | 2.2 | 3.5 | 1.8 | 1.9 | 1.6 | 1.7 | 2.0 | 1.7 | 1.3 |

\* EF = enrichment factor (calculated as ratio of element content in the nodules to that in the matrix).

Ti. The nodules were also enriched in all trace elements determined. The EFs for trace elements decreased in the following order:



from 13.8 for Ba to 1.5 for V. The nodules were enriched in all REE as well, except perhaps La. Among the REE, enrichment in Ce was the strongest (EF=20.5). When the REE contents of the samples were normalized to the REE average contents in chondrites (data from McDonough and Frey, 1989), a strong positive Ce-anomaly was clearly seen in the nodules, compared to the absence of any anomaly in the matrix (Fig. 1a).

Table 4

Dissolution of the nodules in a control experiment (0.5 M HNO<sub>3</sub>) and by hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), hydroxylamine hydrochloride (NH<sub>2</sub>OH–HCl) and Na-citrate-bicarbonate-dithionite (CBD)

| Element                    | Dissolved, % of total |                               |                        |      |
|----------------------------|-----------------------|-------------------------------|------------------------|------|
|                            | Control               | H <sub>2</sub> O <sub>2</sub> | NH <sub>2</sub> OH–HCl | CBD  |
| <i>Major elements</i>      |                       |                               |                        |      |
| Al                         | <0.1                  | 16.7                          | 11.8                   | 38.9 |
| Fe                         | 0.2                   | 4.3                           | 2.8                    | 70.9 |
| Mg                         | <0.1                  | <0.1                          | <0.1                   | 9.7  |
| Mn                         | <0.1                  | 91.9                          | 95.3                   | 95.8 |
| P                          | <0.1                  | 1.1                           | <0.1                   | 59.4 |
| Ti                         | <0.1                  | 3.7                           | <0.1                   | 11.6 |
| Si                         | 1.0                   | 0.9                           | 1.0                    | 4.9  |
| <i>Trace elements</i>      |                       |                               |                        |      |
| As                         | 0.3                   | 3.0                           | <0.1                   | 68.5 |
| Ba                         | 1.3                   | 97.5                          | 98.0                   | 94.8 |
| Co                         | 7.3                   | 98.0                          | 99.7                   | 99.8 |
| Cr                         | 0.6                   | 3.0                           | <0.1                   | 57.7 |
| Cu                         | 5.2                   | 12.4                          | 12.9                   | 77.6 |
| Ni                         | 1.3                   | 28.7                          | 27.4                   | 78.7 |
| Pb                         | 3.3                   | 89.0                          | 93.1                   | 90.6 |
| V                          | 2.4                   | 27.7                          | 19.4                   | 83.1 |
| <i>Rare earth elements</i> |                       |                               |                        |      |
| La                         | 4.1                   | 63.1                          | nd*                    | nd   |
| Ce                         | 2.2                   | 28.3                          | nd                     | nd   |
| Pr                         | 5.4                   | 59.3                          | nd                     | nd   |
| Nd                         | 6.6                   | 61.4                          | nd                     | nd   |
| Sm                         | 6.7                   | 64.4                          | nd                     | nd   |
| Eu                         | 6.1                   | 96.1                          | nd                     | nd   |
| Gd                         | 7.8                   | 88.1                          | nd                     | nd   |
| Tb                         | 7.7                   | 76.4                          | nd                     | nd   |
| Dy                         | 5.6                   | 63.3                          | nd                     | nd   |
| Ho                         | 5.3                   | 64.8                          | nd                     | nd   |
| Er                         | 5.4                   | 68.2                          | nd                     | nd   |
| Tm                         | 4.1                   | 52.3                          | nd                     | nd   |
| Yb                         | 4.6                   | 52.5                          | nd                     | nd   |
| Lu                         | 4.8                   | 50.7                          | nd                     | nd   |

\* nd = not determined.

Results of the selective dissolution procedures are summarized in Table 4. Negligible amounts of major elements and small amounts (<8%) of rare earth and other trace elements were dissolved in the control treatment (0.5 M HNO<sub>3</sub> without H<sub>2</sub>O<sub>2</sub>). Almost complete (>90%) release of Mn was achieved by H<sub>2</sub>O<sub>2</sub> and NH<sub>2</sub>OH–HCl compared to low release (<5%) of Fe and moderate (12–17%) release of Al. Almost complete (>95%) release of Mn was achieved by CBD. Release of Fe, however, was incomplete (70%) in this case. Increasing the stirring time up to 3 h and doubling the solution/solid ratio did not lead to any increase in the amount of Fe released by CBD (data not shown). Considerable amounts of Al (38.9%) and P (59.4%) were released by CBD (1 h treatment).

The percentages of release of trace elements (as well as P) vary significantly among different elements and among different reagents (Table 4). Almost complete (>90%) release of Ba, Co, and Pb was achieved by all 3 procedures used. Low release (<3%) of P, As and Cr, and moderate release (<30%) of Cu, Ni and V was achieved by H<sub>2</sub>O<sub>2</sub>. Similar results were obtained by NH<sub>2</sub>OH–HCl, except that release of P, As and Cr was below the limit of detection (<0.1%). Higher percentages of trace elements were released by CBD: release of >70% was achieved for all trace elements, except for slightly lower values for P, As and Cr.

For rare earth elements, release of >50% was achieved by H<sub>2</sub>O<sub>2</sub> for all elements determined, except for Ce (28%) (Table 4). A strong positive Ce-anomaly was observed in the solution resulting from H<sub>2</sub>O<sub>2</sub> treatment of the nodules similar to that in the nodules itself (Fig. 1b).

## 4. Discussion

### 4.1. Selectivity of the dissolution methods

Some dissolution of Al-containing minerals (gibbsite and kaolinite) was expected to occur in the case of the control experiment (0.5 M HNO<sub>3</sub> without H<sub>2</sub>O<sub>2</sub>) due to strongly acidic reaction of the medium. Non-detectable Al release occurred in this control experiment (Table 4) due, most probably, to the short (30 min) duration of the acid treatment.

The NH<sub>2</sub>OH–HCl and H<sub>2</sub>O<sub>2</sub> methods were expected to completely dissolve Mn oxides without significant dissolution of Fe oxides (Neaman et al., 2004). Results obtained confirmed high selectivity of these two methods with regard to dissolution of Fe (Table 4). Moderate (12–17%) release of Al obtained by these two methods can be explained by (1) increase of accessibility to the surfaces of Al-containing minerals (gibbsite and kaolinite) due to dissolution of Mn oxides, and (2) release of Al from lithiophorite. Assuming that all the Mn in the sample is present in the form of lithiophorite

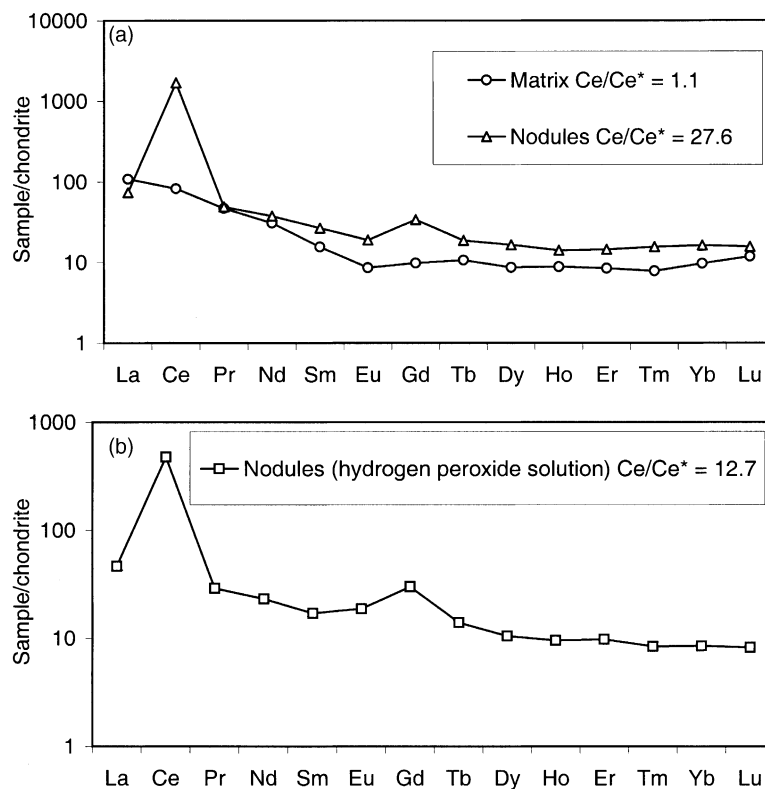


Fig. 1. Chondrite-normalized REE patterns: (a) strong positive Ce-anomaly in the nodules and absence of any anomaly in the matrix; (b) strong positive Ce-anomaly in the solution resulting from  $\text{H}_2\text{O}_2$  treatment of the nodules.  $\text{Ce}^*$  is interpolated linearly between La and Pr.

$\text{LiAl}_2(\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}})\text{O}_6(\text{OH})_6$ , nearly half (49%) of the total Al is present in the form of this mineral.

The CBD procedure was expected to completely dissolve both Fe and Mn oxides. As reported by Cornell and Schwertmann (1996), incomplete release of Fe oxides by the CBD procedure arises from the limited accessibility of their surfaces due to the association of Fe oxides with other minerals, i.e. cementation of other minerals (such as gibbsite and kaolinite) by Fe oxides. This, most probably, was the reason in the present study as well, in spite of the fine grinding of the sample. Considerable (39%) release of Al obtained by CBD can be explained by (1) release of Al from lithiophorite as in the case of  $\text{H}_2\text{O}_2$  and  $\text{NH}_2\text{OH}\text{-HCl}$ , and (2) some (up to 20%) of Al substitution in the structure of Fe oxides. A calculation can demonstrate that 20% Al substitution in the structure of Fe oxides is equal to 39% of the total Al content of the sample. Dissolution of Al-containing minerals (gibbsite and kaolinite) by CBD is not expected to be significant at near neutral pH.

#### 4.2. Associations of trace elements with Mn and Fe oxides

Results obtained indicate that: (1) P, As, and Cr associate mainly with Fe oxides, (2) Cu, Ni, and V

associate with both Fe and Mn oxides, (3) Ba, Co, and Pb associate mainly with Mn oxides (Table 4).

Several different mechanisms can be involved in the association of trace elements with Mn and Fe oxides. Arsenate ( $\text{AsO}_4^{3-}$ ) and phosphate ( $\text{PO}_4^{3-}$ ) are known to be chemisorbed by Fe oxides (e.g., McBride, 1994); Cr(III) is known to substitute readily for Fe(III) in Fe oxide structures (e.g., Cornell and Schwertmann, 1996). Association of Cu, Ni and V with both Fe and Mn oxides involves, most probably isomorphous substitution in the case of Fe oxides (e.g., Cornell and Schwertmann, 1996) and adsorption (ion exchange with release of proton) in the case of Mn oxides (e.g., McKenzie, 1979, 1980). Cobalt has so-called "specific affinity" to Mn oxides (McKenzie, 1970), a mechanism involving oxidation of Co(II) to Co(III) (Murray and Dillard, 1979; Manceau et al., 1997). Adsorption of Pb on Mn involves a mechanism of strong specific adsorption, however, without oxidation of Pb into  $\text{Pb}^{\text{IV}}\text{O}_2$  on Mn oxide surfaces (McKenzie, 1979).

Close association of Ba with Mn oxides found in the present study (Table 4) involves, most probably, the mechanism of co-precipitation of Ba with Mn in a form of hollandite ( $\text{BaMn}_8\text{O}_{16}$ ) since a small diffraction peak at 3.1 Å was detected by XRD analysis. This peak,

however, can be attributed also to coronadite ( $\text{PbMn}_8\text{O}_{16}$ ). Thus, there is a possibility that hollandite and coronadite are present in the nodules.

Results of the present study with regard to the close association of Co, Pb, and Ba, as well as Ni to some extent, with Mn oxides are in accordance with findings reported in the literature. Association of Co with Mn oxides was documented by Taylor and McKenzie (1966), Taylor (1968), Adams et al. (1969), and Golden et al. (1993). Childs (1975) reported that Co and Ba were associated with Mn-rich phases. Associations of Ba with Mn were reported by Ross et al. (1976) and White and Dixon (1996). Zaidelman and Nikiforova (1998) reported accumulation of Co and Pb in Mn nodules. Correlations of Ba, Pb, and Ni contents with Mn contents in Mn nodules were reported by Oliveira et al. (2001). Vaniman et al. (2002) reported associations of Ni, Ba, and Pb with Mn oxides. Substitution of Mn(III) by Ni(II) in the lithiophorite structure has been reported by Manceau et al. (2002).

#### 4.3. Rare earth elements (REE)

REE have very similar chemical properties, which tend to vary gradually along the group. The majority of REE exist in a trivalent state. There are two exceptions to this: (1) under reducing conditions, Eu may exist in the divalent state, and (2) under oxidizing conditions, Ce may be oxidized to Ce(IV) (e.g. McLennan, 1989).

Results of the present study indicate that a positive Ce-anomaly is related to Fe–Mn-nodules (Fig. 1a) where 28% of the Ce was associated with Mn (Table 4). Cerium-anomalies are well known in the marine environment associated with the formation of Mn nodules (e.g., McLennan, 1989). In the continental environment, Rankin and Childs (1976) reported that a preferential enrichment of Ce was related to Fe–Mn nodules in some New-Zealand lateritic soils. Braun et al. (1990) reported, however, that Ce and Fe were behaving differently within lateritic profiles in Cameroon and ascribed positive Ce-anomalies to the deposition of Ce as very insoluble cerianite ( $\text{CeO}_2$ ) under oxidizing conditions, the other REE remaining in solution. Vaniman et al. (2002) reported, on the other hand, that Mn oxides have a significant effect on Ce accumulation by a mechanism of oxidation of Ce(III) to Ce(IV) on Mn oxide surfaces.

#### 4.4. Use of the improved selective dissolution methods in sequential extraction schemes

The improved selective dissolution methods used in the present study are proposed to be included in sequential extraction schemes for fractionation of trace elements in soils and sediments. Each method, however, has its own advantages and limitations as discussed below.

As the first step of dissolution by  $\text{H}_2\text{O}_2$  is oxidation (Neaman et al., 2004), this method is not expected to dissolve Fe oxides, unless some Fe is incorporated into the structure of Mn oxides. However, Al-containing minerals (such as gibbsite) can be partly dissolved by this method, since acid is required to achieve complete dissolution. In addition, most soil organic matter and sulfides would be oxidized by  $\text{H}_2\text{O}_2$ . As a consequence, metallic elements, which form complexes with organic matter and/or associated with sulfides, may be released into solution. This can limit studies of associations of trace elements with Mn oxides if much organic matter and/or sulfides are present.

It is not expected that  $\text{NH}_2\text{OH-HCl}$  will dissolve significant amounts of Al-containing minerals because the pH of the solution is 3.6. Neither is dissolution of soil organic matter likely to occur with  $\text{NH}_2\text{OH-HCl}$ . However, the method is expected to have a weak selectivity if poorly-crystalline Fe oxides are present in large amounts (Neaman et al., 2004).

Thus, either of the two methods can be used depending on organic matter and sulfide contents and crystallinity of Fe oxides.

## 5. Conclusion

The improved selective dissolution methods achieved almost complete release of Mn from the sample without decreasing the selectivity of dissolution, i.e., without dissolving significant amounts of Fe oxides and other minerals, and provided reliable information on associations of trace elements with Mn oxides. These methods are thus proposed to be included in sequential extraction schemes for fractionation of trace elements in soils and sediments.

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