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# Trace element associations with Fe- and Mn-oxides in soil nodules: Comparison of selective dissolution with electron probe microanalysis

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## Abstract

Selective dissolution methods have been largely used to get insight on trace element association with solid phases. Modern instrumental techniques offer many tools to test the validity of selective dissolution methods and should be systematically used to this end. The association of trace elements with Fe- and Mn-oxides in soil nodules has been studied here by electron probe microanalysis. The results were compared with findings from an earlier study on selective dissolution of the same nodules by hydroxylamine hydrochloride, acidified hydrogen peroxide, and Na-citrate-bicarbonate-dithionite. Electron probe microanalysis results were consistent with previous findings using selective dissolution and showed that P, As and Cr were mainly present in Fe-oxides, while Co was mainly associated with Mn-oxide phases. These results support the applicability of the studied selective dissolution methods for fractionation of trace elements in soils and sediments containing appreciable amounts of Fe and Mn-oxide phases.

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## 1. Introduction

Selective dissolution methods and sequential extraction schemes are commonly used in the deter-

mination of trace element associations in soils and sediments (Tessier et al., 1979). However, widespread and uncritical use of such methods and schemes has called into question their validity (Martin et al., 1987; Nirel and Morel, 1990). To test their validity, modern instrumental techniques are generally used (Guest et al., 2002; La Force and Fendorf, 2000). Among these techniques, electron probe

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microanalysis (EPMA) is particularly suitable for chemical analyses of trace elements in isolated soil particles (Amonette, 2002).

Recently, the authors proposed two improved methods for selective dissolution of Mn-oxides that use hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\text{--HCl}$ ) and acidified hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). It was suggested that either of the two methods can be used depending on organic matter and sulfide concentrations and crystallinity of Fe-oxides (Neaman et al., 2004b). Furthermore, these methods were used, together with the classical Na-dithionite-citrate-bicarbonate (DCB) method of Mehra and Jackson (1960), to determine the associations of trace elements with Fe- and Mn-oxides in nodules from a tropical soil (Neaman et al., 2004a). Hydroxylamine hydrochloride and acidified  $\text{H}_2\text{O}_2$  dissolved Mn-oxides without significant dissolution of Fe-oxides, while DCB dissolved both Mn- and Fe-oxides (Trolard et al., 1995).

In the present study, EPMA was used to determine the associations of trace elements with Fe- and Mn-oxides in soil nodules thus testing the validity of the above-mentioned chemical methods for selective dissolution of trace elements associated with Fe- and Mn-oxides in the same nodules.

## 2. Materials and methods

Nodules collected from a tropical soil in Serra do Navio (Northern Brazil) were used in this study and in a previous study by Neaman et al. (2004a). Two intact nodules about 2 mm in diameter were impregnated in epoxy resin and polished before the analysis. Electron probe microanalysis was performed using a Cameca SX50 with four wavelength dispersive spectrometers operated at 15 keV and 80 nA.

The following counting times were used: 10 s for Na, Mg, Si, Ca, K, Al, Fe, Mn and Ti, 90 s for As, Ba, Co and Pb, and 60 s for Cr and P. The following reference materials were used for calibration. Glasses K919 (Ba, Co and Cr) and K493 (Pb) were obtained from the United States National Institute of Standards and Technology. Albite (Al, Si, Na), olivine (Mg), diopside (Ca), K-feldspar (K), apatite (P), garnet (Mn), fayalite (Fe), sphene (Ti) and ardennite (As) were distributed by the Smithsonian Institution and United States Geological Survey as EPMA standards. For trace element analysis, samples and standards were carefully checked to avoid any systematic error due to overlap at peak and background positions. Spot sizes used for the anal-

ysis were approximately 5  $\mu\text{m}$  diameter. The limits of detection were calculated based on counting statistics, and the limit of detection computed as  $\text{LOD} = 3 \times$  standard deviation of counting precision (ACS Committee, 1980).

First, the whole area of each of two nodules (about 2 mm in diameter) was surveyed using backscatter electron images and concentrations of Si, Al, Mg, Ca, Na, K, Fe, Mn and Ti were determined. This allowed identification of Fe- and Mn-oxide phases that differed in brightness in the backscatter electron images. For instance, dark gray areas were clay phases, opaque gray areas were Mn-oxide phases, while bright gray areas were Fe-oxide phases (Fig. 1). Then, spots for analysis of trace elements were individually selected from real time backscatter electron images. The concentrations of Al, Mn, Fe, Ti, P, As, Cr, Ba, Co and Pb were determined in Fe- and Mn-oxide phases. Table 1 presents results for the two nodules analyzed. For bulk chemical analyses and selective dissolution, a number of nodules was crushed and homogenized (Neaman et al., 2004a, Tables 2 and 3).

## 3. Results and discussion

X-ray diffraction analyses showed (Neaman et al., 2004a) the nodules to be composed of kaoli-

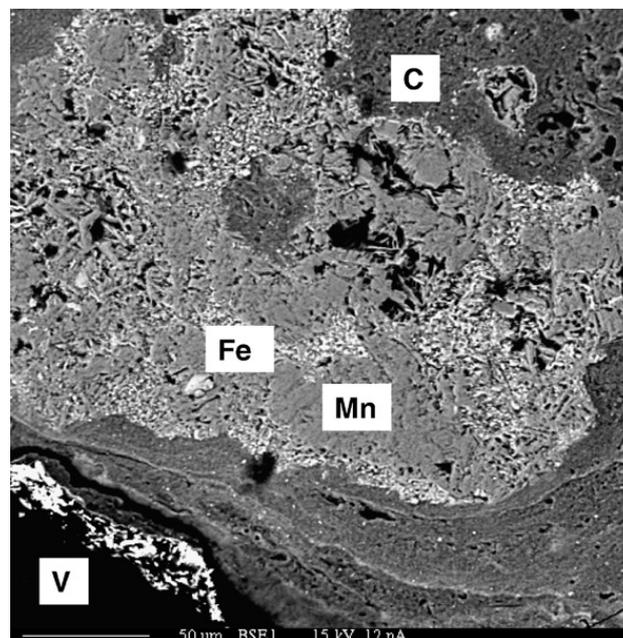


Fig. 1. Backscatter electron image of an area from one individual intact nodule. Dark gray areas are clay phases (C); opaque gray areas are Mn-oxide phases (Mn), bright gray areas are Fe-oxide phases (Fe), and black areas are void spaces (V). The image is 512  $\times$  512 pixels.

Table 1  
Chemical composition of oxides studied by EPMA<sup>a</sup>

As, mg/kg	Co, mg/kg	Cr, mg/kg	P, mg/kg	Al, %	Ti, %	Mn, %	Fe, %
<i>Fe-oxides</i>							
10790	510	420	640	2.06	0.22	1.45	57.58
930	bdl	11900	540	3.69	0.27	bdl	56.85
670	bdl	980	250	2.20	0.83	3.51	57.28
1190	bdl	13900	730	4.43	0.12	0.09	55.66
9300	2400	bdl	nd	1.97	0.10	4.81	54.18
13310	1590	210	nd	2.39	0.21	3.85	55.45
740	bdl	11470	nd	4.63	0.10	0.18	57.50
4580	2140	bdl	nd	4.68	0.19	11.44	44.97
<b>5189</b>	<b>830</b>	<b>4860</b>	<b>540</b>	<b>3.26</b>	<b>0.26</b>	<b>3.17</b>	<b>54.93</b>
<i>Fe-Ti-oxides</i>							
220	bdl	bdl	bdl	0.17	33.09	3.82	20.45
bdl	270	430	bdl	bdl	31.01	1.54	28.29
bdl	bdl	bdl	bdl	bdl	30.39	3.50	32.42
bdl	bdl	990	bdl	bdl	29.45	2.87	31.97
620	220	900	bdl	3.01	29.28	4.49	22.33
bdl	bdl	360	nd	bdl	29.00	3.18	32.95
<b>140</b>	<b>82</b>	<b>447</b>	<b>bdl</b>	<b>0.53</b>	<b>30.37</b>	<b>3.23</b>	<b>28.07</b>
<i>Mn-Al-oxides</i>							
bdl	670	bdl	bdl	11.47	0.01	37.55	0.10
bdl	1450	bdl	bdl	12.08	0.04	37.00	0.06
bdl	bdl	bdl	nd	12.09	0.32	35.25	5.06
bdl	500	bdl	nd	11.53	0.22	36.18	3.98
bdl	320	bdl	nd	11.89	0.27	35.84	4.49
bdl	bdl	bdl	nd	11.54	0.23	35.61	3.08
bdl	220	bdl	nd	11.93	0.17	36.42	1.70
<b>bdl</b>	<b>451</b>	<b>bdl</b>	<b>bdl</b>	<b>11.79</b>	<b>0.18</b>	<b>36.26</b>	<b>2.64</b>
<i>Calculated detection limit</i>							
177	188	189	268	0.01	0.02	0.05	0.05

<sup>a</sup> bdl = below the detection limit; nd = not determined. Average values are given in bold; “bdl” values being considered as zero.

nite, gibbsite, goethite, hematite, quartz and 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). Iron- and Mn-oxide phases were detected by EPMA (Table 1). The composition of Mn-oxides is consistent with the stoichiometry of lithiophorite (12.7% of Al and 38.9% of Mn). The composition of Fe-oxides is consistent

with the stoichiometry of goethite (62% of Fe) with some substitution of Fe by Al, Mn and Ti ( $\text{Fe}_{0.84}\text{Al}_{0.10}\text{Mn}_{0.05}^{\text{III}}\text{Ti}_{0.01}\text{OOH}$ ). The Fe–Ti-oxide phases detected by EPMA (Table 1) are considered to be minor since the concentration of  $\text{TiO}_2$  in bulk nodules is 1.11% (Table 2). In addition, the Fe–Ti-oxide phases did not contain considerable concentrations of any trace element (Table 1).

EPMA analyses indicate that As and Cr were mainly present in Fe-oxides in local concentrations up to 13,300 mg/kg and 13,900 mg/kg, respectively (Table 1). Given the  $\text{Fe}_2\text{O}_3$  concentration of 42%, As concentration of 1250 mg/kg, and Cr concentration of 2770 mg/kg in bulk nodules (Table 2), the average concentrations of As and Cr in the Fe-oxides are expected to be 3000 mg/kg and 6500 mg/kg, respectively. Thus, the average EPMA results for As and Cr (5190 and 4860 mg/kg, respectively) are of the same order of magnitude as expected from the chemical analysis of bulk nodules.

Phosphorus was also mainly present in Fe-oxides, with concentrations up to 730 mg/kg (Table 1). Although some phases with considerably larger concentrations of P were expected to occur based on the P concentration in bulk nodules (Table 2, 13,760 mg/kg or 0.32% of  $\text{P}_2\text{O}_5$ ), none were detected by EPMA.

Selective dissolution analyses of bulk nodules suggested that P, As and Cr are associated mainly with Fe-oxides (Table 3). Results of the present study are consistent with these findings and thus validate the applicability of the method of Mehra and Jackson (1960) and those of Neaman et al. (2004a,b), in the determination of the associations of trace elements with Fe- and Mn-oxides.

Cobalt has so-called “specific affinity” to Mn-oxides (McKenzie, 1970), a mechanism involving oxidation of  $\text{Co}^{\text{II}}$  to  $\text{Co}^{\text{III}}$  (Manceau et al., 1997; Murray and Dillard, 1979). Although selective dissolution analyses of bulk nodules suggested that Co is associated mainly with Mn-oxides (Table 3),

Table 2  
Elemental composition of bulk nodules, in weight percent for major and minor elements and in mg/kg for trace elements (based on Neaman et al., 2004a)

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	MnO	MgO	$\text{K}_2\text{O}$	$\text{TiO}_2$	$\text{P}_2\text{O}_5$	LOI <sup>a</sup>	Total
14.67	12.55	41.88	13.00	0.22	0.32	1.11	0.32	13.72	97.79
Pb	Ba	As	Co	Cr					
357	2435	1252	216	2771					

Concentrations of CaO and  $\text{Na}_2\text{O}$  are <0.01%.

<sup>a</sup> LOI = loss on ignition.

Table 3  
Dissolution of bulk nodules by H<sub>2</sub>O<sub>2</sub>, NH<sub>2</sub>OH–HCl and Na-dithionite-citrate-bicarbonate (DCB). Based on Neaman et al. (2004a)

Element	Dissolved, % from total		
	H <sub>2</sub> O <sub>2</sub>	NH <sub>2</sub> OH–HCl	DCB
Fe	4.3	2.8	70.9
Mn	91.9	95.3	95.8
P	1.1	<0.1	59.4
As	3.0	<0.1	68.5
Ba	97.5	98.0	94.8
Co	98.0	99.7	99.8
Cr	3.0	<0.1	57.7
Pb	89.0	93.1	90.6

EPMA results indicated that Co is associated with both Fe- and Mn-oxides (Table 1). However, it was noted that the highest Co concentrations in Fe-oxide-rich areas are associated with Mn-rich phases, except for one spot with a Mn concentration of 3.51% where Co concentration was below the detection limit (Table 1). Thus, it is likely that Co was associated with Mn-oxide phases.

It could be argued that the latter Co-enriched phases are Fe-oxides with a large degree of isomorphous substitution of Fe by Mn. However, this possibility is not likely because almost complete (>90%) release of Mn was achieved by H<sub>2</sub>O<sub>2</sub> and hydroxylamine hydrochloride in comparison with minor (<5%) release of Fe (Table 3). It is well known that Al and Cr substitute for Fe in goethite (Cornell and Schwertmann, 1996; Schulze, 1984; Schwertmann et al., 1989; Trolard et al., 1995). In contrast, Mn in goethite forms phylломanganate clusters, either asbolane, lithiophorite or hexagonal birnessite, as evidenced by EXAFS (Manceau et al., 2000). Moreover, Co-EXAFS showed all Co atoms were associated with the phylломanganate clusters, partly substituted in the layer and partly sorbed in the interlayer.

This framework of interpretation can be extended to the present study: Co could be either directly associated with Mn-oxides, or associated with phylломanganate clusters in goethite, but not directly substituted for Fe in goethite. This would reconcile both of the observations: (i) Co is geochemically associated with Mn-oxides, since >98% Co is extracted by hydroxylamine hydrochloride and H<sub>2</sub>O<sub>2</sub>, chemicals that do not dissolve Fe-oxides (Table 3); (ii) the highest Co concentrations obtained by EPMA are observed in Fe-oxide-rich areas and correlated with Mn concentrations in the same spots (Table 1). Most probably, both Fe-

and Mn-oxide phases were analyzed together by EPMA in these spots. Thus, the data obtained by EPMA analysis are consistent with selective dissolution results in regard to Co association with Mn-oxides.

It was not possible to compare EPMA results for Pb and Ba with the results of selective dissolution analyses (Neaman et al., 2004a) because the concentrations of Pb and Ba were below the limit of detection (820 and 630 mg/kg, respectively) in all oxide phases. This was expected for Pb considering that its concentration is 357 mg/kg in bulk nodules (Table 2). In contrast, phases with Ba concentrations considerably higher than the limit of detection were expected based on the Ba concentration of 2435 mg/kg in bulk nodules (Table 2). The presence of hollandite (BaMn<sub>8</sub>O<sub>16</sub>) in the nodules is thus not excluded, and the small X-ray diffraction peak at 3.1 Å could be ascribed to this mineral (Neaman et al., 2004a). However, no hollandite was detected by EPMA. Thus, it was not possible to validate the findings of selective dissolution methods with regard to Pb and Ba associations with Mn-oxides.

#### 4. Conclusions

Electron probe microanalysis (EPMA) results were, in general, consistent with the findings of chemical selective dissolution analyses with regard to the associations of trace elements with Fe- and Mn-oxides in soil nodules. Considering that only two nodules were analyzed in the present study, further studies are necessary to validate whether the methods of Mehra and Jackson (1960) and Neaman et al. (2004a,b) would be valid for fractionation of trace elements in soils and sediments containing appreciable amounts of Fe- and Mn-oxide phases.

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