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# Rare Earth Elements in Soil on Spoil Heap of an Abandoned Lead Ore Treatment Plant in the District of Mfouati, Congo-Brazzaville

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#### Abstract

The aim of this study was to assess the vertical migration of rare earth elements (REE) in a soil profile. Rare earth elements, reference elements (Ti, Fe, Mn and Al) and soil characteristics (pH, organic matter, sulphate and granulometry) of a soil profile on spoil heap were measured in 54 soil samples divided into five composite samples at different depths: 15-45 cm, 45-75 cm, 75-105 cm, 105-135 cm and 135-150 cm. The first 15 cm of the top layer contained an accumulation of ore were not sampled. Low rare earth elements (LREE) and high rare earth elements (HREE) contents in the soil profile decreased from 91.74 to 14.06 mg/kg and 9.01 to 4.05 mg/kg, respectively. High positive correlations were observed between REE fractionation and organic matter, sulfate and the reference elements in the studied soil profile. A high soil acidity promotes the REE fractionation. The chondrite-normalized REE patterns in the soil profile were characterized by LREE enrichment and negative anomalies of cerium and terbium, which are mainly controlled by complexing with sulphate and organic matter, adsorption on Fe/Mn oxyhydroxydes and clay minerals.

Keywords: Rare earth elements spoil heap, migration.

## Introduction

REE (rare earths elements) constitute a group of elements (from La to Lu) characterized by similar chemical and physical properties (e.g., the ionic radius), the valence state +3, with the exception of cerium and europium which strongly depend on the redox potential<sup>1</sup>. Many studies have indicated the importance of REE as geochemical tracers in the understanding and the description of the chemical evolution of the earth's continental crust<sup>2-4</sup> and the origin of sediments <sup>5</sup>. In the soil, the behavior of REE is generally similar to that of trace metals, thus the main characteristics of the soil such as clay fraction, organic matter can provide a greater reserve of these elements<sup>6</sup>. Organic matter and pH are as important features of the soil composition<sup>7</sup>. The retention of REE is mainly controlled by the following factors: the stability of the primary REE-carrying minerals, the presence of secondary phases such as clays, Fe and Mn oxyhydroxides<sup>8,9</sup>, the organic matter content<sup>10, 11</sup> and the inorganic anions chloride, sulfate, phosphate<sup>12</sup>. During weathering and the processes above-mentioned, the rare earth elements may be mobilized, undergo a fractionation<sup>13</sup> and be incorporated in clay minerals<sup>14</sup>.

In the south eastern Congo Brazzaville, a treatment plant of non-ferrous metals (Pb, Zn and Cu) of which the activity was to concentrate lead, involve crushing of ore rich in metals followed by disposal of metal-bearing rock as mine tailings. The treatment plant was abandoned since the Eighties. The objectives of this work were to study the distribution of REE in the soil profile on spoil heap and to determine the factors controlling their distribution. The contents of REE, reference elements (Ti, Fe, Zr and Mn), sulphate and organic matter with other soil characteristics were determined, aiming at the comprehension of the migration of REE in the soil profile. The aim is relevant, because the abandoned treatment plant of lead ore remains a continual source of acid mine drainage (AMD) and metal contamination. Soils and watercourses in the study area are still highly polluted. For this research, the analytical technique employed was Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for the analysis of REE and reference elements in the soil profile.

## **Material and Methods**

**Study area:** The site retained for sampling was the spoil heap of an abandoned treatment plant in Mfouati (south east Congo-Brazzaville), which activity was stopped for more than twenty years. The ore treatment plant was built on the side of a hill located at 442 m of altitude between 367178.59-370507.20 UTM south latitude and 9512957.94-9515800.06 UTM east longitude. The annual rainfall varies from 1050 to 1650 mm. The soils are of ferralitic type, which have been derived from schisto-limestone.

**Sampling:** Five composite soil samples were collected in a soil profile of the spoil heap in the vicinity of the abandoned treatment plant, at depth intervals of 15-45, 45-75, 75-105, 105-135 and 135-150 cm, using steel stainless. The sampling period was August 2008 (dry season). The first 15 cm was not sampled because of an accumulation of ore. The soil profile showed no

distinct horizons. After sampling, the composite soil samples were packed in different polyethylene bags to prevent exposure to air. Sample location is presented in figure-1.

Analytical: REE were analyzed by ICP-MS at the Centre de Géochimie de la Surface (Strasbourg, France) in the bulk samples. A mass of 0.1g of each homogenized composite soil sample was digested by triacid attack (HF-HCO<sub>4</sub>-HNO<sub>3</sub>) in a Teflon vessel and heated in a microwave oven at 180°C for 10 min. The digested solution was diluted to a known volume with double distilled water, and then it was analyzed for REE by ICP-MS. The contents of anions  $SO_4^{2-}$  was determined by ionic chromatography and coulometric detection. The principal properties of soil were determined, such as CEC (Metson method), organic matter (OM) (standard method NF ISO 10694), and granulometry three fractions (Robinson pipette). Soil pH was measured in the proportion 1:2 (soil/water) using a Hanna pH-meter with combined electrodes after calibration with two buffer solutions, pH 7 and 4. The anions sulphate was determined using ionic chromatography DIONEX model IC25.

## **Results and Discussion**

The main characteristics of the soil profile are shown in table-1. The soil profile has an acidic nature with the pH values ranged from 5.69 to 6.15. The CEC values ranged from 2.90 to 3.54 cmol/kg. The concentration of sulphates which derived from the oxidation of sulfides minerals (pyrite, galena, and chalcopyrite) decreased in the soil profile from 179 to 104 mg/kg. Reference element contents Fe, Zr and Mn decreased with depth as 53130 -18620, 90 - 38 and 6700 - 750 mg/kg, respectively. The percentage of TiO<sub>2</sub> decreased also in the soil profile from 0.26 to 0.11%. Organic matter contents decrease from 2.76 to 1.62 g/kg. On the other hand, clay contents in the soil profile increase from 325 to 344 g/kg. A previous study showed that the clay fraction in the soil profile was constituted predominantly of talc, followed by kaolinite, smectite and chlorite in very small quantities<sup>15</sup>. The REE data measured in the soil profile together with  $\Sigma REE$ , the fractionation index  $(La/Yb)_{ch}$ , the anomalies in cerium (Ce/Ce\*)<sup>16</sup> and terbium (Tb/Tb\*)<sup>17</sup> are given in table-2. The chondrite data<sup>18</sup> used for normalizing the REE contents (mg/kg) in the soil profile are also listed in table-2. The REE patterns in the soil profile show a decrease in the REE contents and are similar at different depths, with a negative Ce and Tb anomalies (figure-2). The negative cerium and terbium anomalies varied from 0.79 to 0.63 and from 0.57 to 0.46, respectively. Cerium is very sensitive to redox conditions<sup>19, 20</sup>. In the study area, the rains cause a hydromorphy of the soil and favor the oxidizing conditions. The ions  $Ce^{3+}(aq)$  are released and oxidized to  $Ce^{4+}$ . In the soil profile, Ce anomalies have a strong correlation with terbium anomalies (figure-3), these associations suggest that the two types of anomalies are induced by the same processes. In oxidizing conditions, the cerium anomalies are caused by the precipitation of Ce in cérianite  $(CeO_{2(s)})^{21}$  and also by successive decomposition of organic matter <sup>22</sup>. As for terbium anomalies, they may result from the decomposition of organic matter in the soil profile. Significant decomposition of organic matter decreases the ability to transfer insoluble elements in aqueous solution, which causes the precipitation of REE with organic matter <sup>22</sup>. A strong correlation was found between the cerium and terbium anomalies with organic matter (figure-4).

REE fractionation and pedogenic processes: The evolution of REE fractionation with respect to the soil profile characteristics, major elements Fe, Mn, Zr, and percentage of TiO<sub>2</sub> is shown in figure-5. Lower is the pH value, higher is the REE fractionation. It is the same for the role of clays in the fractionation of REE. Thus, high soil acidity promotes the fractionation of rare earth elements in this soil profile. Equilibrium release experiments of some REE (La, Ce, Gd and Y) demonstrated the increasing of the release with decreasing pH<sup>23</sup>. On the other hand, more the concentration of Fe, Mn, O.M and SO<sub>4</sub><sup>2-</sup> increases in the soil profile, more the REE fractionation expressed by the ratio (La / Yb)<sub>ch</sub> increases. The high relationship between O.M and REE shows also that REE are complexed by organic matter. The strong correlation between REE contents in the soil profile and Mn, Fe contents suggests that REE might originate from the dissolution of Fe/Mn oxyhydroxides in low soil pH<sup>23</sup>. Some studies have highlighted the pH-dependence of REE complexation by humic acid and explain the process by the deprotonation of humic acid carboxylic and phenolic surface groups at increasing pH<sup>24, 25</sup>. A strong correlation was found between Fe contents and O.M (r = 0.96) in the soil profile, which denotes that iron (III) oxyhydroxides were linked to OM. Thus, the REE mobility in the soil profile was controlled by the dynamic of OM and Fe/Mn oxyhydroxides.

Organic matter and oxyhydroxides of Fe/Mn are REE vectors of mobility in the soil profile. Several studies have shown that iron oxides are in the form of nodules which are constituted of goethite or hematite, sometimes of ferrihydrite  $^{26-28}$ . In tropical soils, hematite is present in these nodules. Cerium (Ce<sup>4+</sup>) has been found by SEM-EDS in the iron-rich nodules <sup>29</sup>. The X-ray diffraction of composite soil samples has revealed the presence of hematite and goethite in the soil profile. The sum of REE shows a strong association with inorganic complexing  $SO_4^{2-}$ . Similarly the abundances of rare earth elements, expressed as the La concentration, have a strong correlation with Zr and TiO<sub>2</sub> contents in the soil profile (figure-6 b-c). In the soil profile, the metals Zr and Ti can be associated with the heavy minerals  $ZrSiO_4$  and  $CaTi(SiO_4)$ , respectively. These minerals carry also REE. The relationships La-Zr and La-TiO<sub>2</sub> have been already highlighted in the sediments <sup>30</sup>

## Conclusion

The principal findings are: i. In the studied soil profile, the REE fractionation was marked by an enrichment of LREE (La – Eu) relative to HREE (Gd – Lu), ii. The relationships identified between REE and the soil characteristics show that the pH control the processes such as REE complexation with organic

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matter (humic substances) and inorganic anions sulphate, adsorption / desorption of REE on the surface of clay minerals and inorganic colloids (oxyhydroxides of Fe, Mn), precipitation of Ce., iii. Cerium and terbium anomalies are controlled by acid pH, iv. Fe colloids (oxyhydroxides) were linked to OM, v. REE mobility in the soil profile was controlled by the dynamic of OM, iron/manganese oxyhydroxides and sulphates, vi. The potential of REE to be used as a tracer of the soil phases involved in the processes running in the soil profile on spoil heap.

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Depth	pН	CEC	SO4 <sup>2-</sup>	Fe	Zr	Mn	TiO <sub>2</sub>	Sand	Silt	Clay	O.M.
(cm)		(cmol/Kg)	(Mg/Kg)			(%)	(g/Kg)				
15-45	5.69	2.90	179	53130	90	6700	0.26	306	370	325	2.76
45-75	6.10	2.91	168	41440	74	3400	0.21	268	400	333.2	2.61
75-105	6.04	3.11	167	23590	44	2500	0.14	258	400	343	1.99
105-135	6.25	3.30	110	21210	46	700	0.13	239	408	353	1.98
135-150	6.15	3.54	104	18620	38	750	0.11	145	421	344	1.62

 Table-1

 Characteristics and Reference Element Content of the Soil Samples

Table-2								
REE data of the soil profile on spoil heap								

	Depth (cm)						
REE	15-45	45-75	75-105	105-135	135-150	Chondrites	
La	31.95	25.41	14.91	13.67	11.00	0.34	
Ce	26.08	19.30	12.96	8.36	6.69	0.91	
Pr	6.46	5.14	3.00	2.73	2.25	0.121	
Nd	22.55	18.23	10.78	9.97	8.31	0.64	
Sm	3.93	3.19	2.00	1.83	1.55	0.195	
Eu	0.77	0.63	0.41	0.37	0.31	0.073	
Gd	2.98	2.40	1.43	1.30	1.08	0.26	
Tb	0.38	0.29	0.16	0.15	0.12	0.047	
Dy	2.41	2.03	1.34	1.33	1.17	0.30	
Но	0.45	0.39	0.26	0.26	0.24	0.078	
Er	1.20	1.01	0.72	0.70	0.65	0.20	
Tm	0.20	0.17	0.12	0.11	0.11	0.032	
Yb	1.22	1.07	0.74	0.71	0.59	0.22	
Lu	0.17	0.15	0.10	0.10	0.09	0.034	
∑REE	100.75	79.42	48.93	41.59	34.15		
(La/Yb) <sub>ch</sub>	1.20	1.16	1.09	1.07	1.05		
Ce/Ce*	0.79	0.76	0.76	0.65	0.63		
Tb/Tb*	0.57	0.56	0.52	0.51	0.46		

 $(La/Yb)_{ch}+(La/La_{ch})/(Yb/Yb_{ch}); Ce/Ce^*=(ce/Ce_{ch})/(La/La_{ch} \ge Pr/Pr_{ch}) \exp 0.5$ 

Tb/Tb\*=  $(Tb/Tb_{ch})/(Gd/Gd_{ch} \times Dy/Dy_{ch}) \exp 0.5$ 



Figure-1 Location of the Spoil Heap in the Study Area



Figure-2 Chondrite-Normalized Ree Patterns for the Soil Profile



Figure-3 Relationship between Ce and Tb anomalies in the soil profile



Figure-4 Relationship between O.M and (a) Ce/Ce\*; (b) Tb/Tb\*







Figure-5 (a-e) Evolution of REE fractionation with soil characteristics and major elements in the soil profile







- a- Relation between inorganic anions  $SO_4^{2-}$  and  $\Sigma REE$
- b- Relation between La and Zr
- c- Relation between La and TiO<sub>2</sub>