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ELEMENTARY CONCENTRATION OF PERUÍBE BLACK MUD BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

The Peruíbe Black Mud is used in therapies such as psoriasis, peripheral dermatitis, acne, seborrhea, myalgia, arthritis and rheumatic non-articular processes. This material is characterized by its fine organic matter particles, sulphate reducing bacteria and a high content of potential reduction ions. Although this material is considered natural, it may not be free of possible adverse health effects, like toxic chemical elements, when used for therapeutic purposes. In the therapeutic treatments involving clays, clays are used in mud form also called peloids, obtained by maturation process. Five *in natura* and three maturated Black Mud samples were collected in Peruíbe city, São Paulo State, Brazil. To investigate the distribution of major, trace and rare earth elements in the *in natura* and maturated clays that constitute the Peruíbe Black Mud, neutron activation analysis (NAA) was used. A comparison between *in natura* and maturated mud shows that the major, trace and rare earth elements follow the same order in both types. Generally, the concentrations in the maturated mud are slightly lower than *in natura* mud. Enrichment on the upper continental crust could be observed for the elements As, Br, Sb and Se, in these types of mud.

Keywords: Peruíbe Black Mud, neutron activation analysis (NAA), *in-natura* mud, maturated mud.

1. INTRODUCTION

The use of minerals for therapeutic purposes is an ancient practice, particularly with regard to clay minerals such as smectite, kaolinite and palygorskite [1-2]. Since a long time ago, clay has been used in wound healing to relieve skin irritation, with anti-inflammatory purpose, and to treat gastrointestinal disorders. Currently, it is also highlighted its use in the pharmaceutical industry, as an active ingredient, due to its high absorption capacity and specific surface, easy handling in pharmaceutical formulations, as excipient, and also because it promotes drug disintegration, influencing the processes of medicine liberation, when orally administered. Furthermore, clay is used as topical cosmetics, owing to its characteristic of adsorbing substances, such as fats and toxins.

Clay is a substance found throughout the earth surface, as it is the main component of soils and pelitic sedimentary rocks. Due to its frequency of occurrence and particular properties, mineral clay has been used as a fundamental component in several medicinal products [3]. The high number of applications using clay is related to the high mineralogical variety this element is found. In this context, therapeutic treatments using clay have acquired increasing economic importance.

In the therapeutic treatments involving clay, its mud form is generally used, composed by a mixture of clay and sea water or mineral medicinal water. This clay and water mixture is usually called peloid. For the peloid obtainment, the clay needs to remain in contact with the water for long periods (about six months): this process is called maturation [4].

In Brazil, the Black Mud, found in Peruíbe city, São Paulo State, has been extensively used for therapeutic treatments. The material located on the banks of Rio Preto, in the plain of Peruibe, accumulated in adjacent dikes during overflow river events, is characterized by its high content of fine particles, organic matter, sulphate reducing bacteria and potential reduction ions [5]. The Peruíbe Black Mud is commonly used in the treatment of psoriasis, dermatitis peripheral, acne and seborrhoea, as well as its use in myalgia, arthritis, and non-articular rheumatic processes. A mineralogical, microbiological and chemical analysis, conducted by the Institute for Technological Research of São Paulo (IPT), determined that the Black Mud is composed by silitic-clay, quartz, halite, phyllosilicates and that the clay minerals, also, present silicon, sulfate, zinc, lead, chromium, nickel and aluminum in its chemical composition. Microbiological analysis revealed the presence of sulfate-reducing bacteria. According to this study, the deposit of Peruibe mud weighs 83 tons, with a depth of 75m, distributed in 5 acres. This makes the city the world's largest continuous natural reservoir, a highlighted touristic place, with great economic potential [6].

Although considered as a natural material, clay is not free of possible adverse health effects when used for therapeutic purposes, mainly due to the occurrence of radioactive or toxic elements or minerals that are dangerous to the respiratory system [7-8]. The objective of this study was to characterize *in-natura* and maturated Peruíbe Black Mud, commonly used in therapeutic treatment, by measuring its elemental concentrations by instrumental neutron activation analysis, determining its moisture, organic matter (OM) and loss of the ignition (LOI) content.

2. METHODS

Five *in natura* and three maturated Black Mud samples were collected in the "Lamário of Peruíbe", in Peruíbe city, São Paulo State, Brazil, in two different periods, one in 2011 and the other in 2012. For the determination of moisture, OM and LOI, the samples were centrifuged and the supernatant was discarded. A precise weighted aliquot of each type of mud was dried in a furnace oven at 105º C, for 24 hours, for moisture determination. The same samples were, then, left to stand in a muffle, at 550º C, for four hours, for OM determination. For LOI determination, the samples were heated in the muffle for two hours, at 1000º C.

For the neutron activation analysis, samples were dried in a ventilated oven at 60º C, till constant weight. After that, they were transferred to a mortar, previously, decontaminated with HNO_3 and crushed into particles sized 200 mesh and homogenized. Approximately 120 mg of samples were packed in polyethylene bags for irradiation, together with Standard Reference Materials (SRM), in the IEA-R1 nuclear reactor at IPEN. The SRM used were Estuarine Sediment, SRM 1646a, from the National Institute of Standards and Technology (NIST), Syenite, Table Mountain, STM, from the United States Geological Survey (USGS) and standard solutions (SPEX CertiPrep), pipeted in paper sheets. The elements As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb, Zn and Zr were determined. Samples and SRM were irradiated for 8 h and counted after 7 to 20 days, depending on the radionuclide half-live produced in the irradiation, under a thermal neutron flux of 1 to 5 x 10^{12} n cm^{-2} s^{-1}. Gamma spectrometry was performed using an EG & G Ortec Ge-Hiperpure detector and associated electronics, with a resolution of 2.04 keV for the 1332 keV gamma transition of ^{60}Co. The concentrations were obtained by comparing the photopeak area of the interested element in the spectrum of the sample with that of the standard reference materials, using the following expression:

$$C_{ai} = \frac{(A_{ai}\ w_p\, C_{pi})e^{-\lambda(ta-tp)}}{A_{pi}\ w_a} \tag{1}$$

where C_{ai} is the element concentration in the sample (in µg g^{-1}); C_{pi} is the element concentration in the SRM (in µg g^{-1}); A_{ai} is the activity of the element in the sample (in counts per second); A_{pi} is the activity of the element in the SRM (in counts per second); w_a e w_p are the weighs of the sample and SRM (in g), respectively; λ is the element decay constant and t_a - t_p is the difference of the counting time between the sample and the SRM. The quality control of the results was done by cross checking the reference materials used in the analysis.

3. RESULTS AND DISCUSSION

Moisture, organic matter and loss on ignition (LOI) results are shown in table 1. A study with several different types of pharmaceutical clay [9] and the results showed moisture, organic matter and loss on ignition varying from 4 to 17%, 3 to 12.5% and 4 to 34%, respectively. Comparing with these results, the *in natura* and maturated Peruíbe black mud showed higher moisture and OM content, while LOI was significantly lower, confirming the richness of Peruíbe Black mud as for organic compounds.

For the methodology precision and accuracy verification, certified reference materials Estuarine Sediment 1646a (ES), from the National Institute of Standards Technology (NIST) and Syenite, Table Mountain (STM), from the United States Geological Survey (USGS) were analyzed. The results are shown in Table 2; it can be observed that good precision and accuracy were obtained for most of the elements, with relative standard deviation (RSD) and relative error (RE), generally, lower than 10%.

Table 1: Contents in % for moisture, organic matter (OM) and loss of ignition (LOI) for black mud samples

Analysis	*In natura*	Maturated
Moisture	49 ± 1	64 ± 2
Organic Matter	11.8 ± 0.4	20 ± 1
Loss on Ignition	1.87 ± 0.07	2.68 ± 0.07

The results obtained for *in-natura* and maturated Peruíbepp Black Mud analysis are shown in Table 3. It can be noted, by the results, that the analyzed clay does not show significant differences in its element concentrations and only some small variations could be observed, indicating that there are no chemical differences between *in-natura* and maturated mud. The results of the analysis showed that the elements As, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Nd, Sc, Sm, Ta, Tb, Th, U, Yb, and Zr varied around 30%, and the elements Br, Rb, Sb, Se and Zn showed variations ranging from 37 to 50%, in the *in-natura* mud. As to the maturated mud, the results varied around 20% for almost all the elements, except Sb and Se that presented larger variation, from 89 and 123%, respectively.

The elements As, Sb and Ba are potentially toxic and Rb, Cr, Zr and the rare earth elements can be considered dangerous [9]; however, there is no regulation for these elements in clay minerals for therapeutic use. According to European regulations, elements such as As, Cd, Hg, Pb, Sb, Se, Te and Tl should be absent in cosmetic products due to their hazardous potential [10]. Consequently, it is important to know the concentration of these toxic metals in the mud used for medical purposes since such metals tend to concentrate in it [8]. Arsenic is ubiquitous in our environment and it is a poison, when in large amounts. It is the third most prevalent element in the earth's crust. Arsenic was declared carcinogen for humans by the International Agency for Research on Cancer (IARC), in 1980. Excessive exposure to this element poses health problems, such as various types of cancer, cardiovascular diseases, diabetes and neurological disorders, as well as dermal effects [11].

Considering the elements addressed in this study, the As concentration in *in-natura* and maturated mud varies from 7.3 to 12 µg g^{-1} and 4.72 to 10 µg g^{-1}, respectively, being approximately three times greater than the Multani Mitti (MM), a type of clay used in Pakistan to geophagy that presents a mean concentration of 2.46 µg g^{-1} [11], and slightly above the mean value for the upper continental crust (UCC) that is 1.5 µg g^{-1} [12].

Table 2: Values obtained in the certified analysis of reference materials for quality control of the results, in μg g^{-1}, except where indicated %

	SRM 1646a				STM			
Elements	Certified Value	Measured Value	RSD	RE	Certified Value	Measured Value	RSD	RE
As	6.23 ± 0.21	6.15 ± 0.33	5.37	1.28				
Ba	210	217. 7 ± 58.3	26.80	3.68	639 ± 61	929.388 ± 245.7	14.42	45.38
Ca(%)	0.52 ± 0.02	0.69 ± 0.06	8.57	34.6	0.78 ± 0.03	0.6 ± 0.8	11.29	20.51
Ce	34	34.9 ± 1.2	3.36	2.53	256 ± 23	257.3 ± 8.5	3.31	0.51
Co	5	4.87 ± 0.06	1.23	2.60				
Cr	40.9 ± 1.9	42.4 ± 1.8	2.76	3.67				
Cs					1.52 ± 0.06	1.5 ± 0.1	7.10	1.97
Eu					3.45 ± 0.25	4 ± 1	2.39	9.28
Fe(%)	2.008 ± 0.039	2.02 ± 0.02	0.99	0.60	3.77 ± 0.09	4.03 ± 0.04	0.99	6.90
Hf					27 ± 0.8	28.7 ± 0.3	1.15	6.48
K(%)	0.86 ± 0.02	ND			0.38 ± 0.17	ND		
La	17	17.1 ± 0.3	1.81	0.65	154 ± 11	152.1 ± 2.7	1.78	1.22
Lu					0.6 ± 0.04	0.67 ± 0.02	2.99	11.67
Na(%)	0.74 ± 0.0017	0.73 ± 0.01	1.37	1.35	6.61 ± 0.68	6.70 ± 0.14	2.09	1.36
Nd	15	11.8 ± 0.9	7,3	21,3	81 ± 4.8	78.3 ± 3.7	4,7	3,4
Rb	38	34.3 ± 1.6	4.55	9.71	114 ± 11	127.4 ± 4.8	3,8	11,8
Sb	0.3	ND						
Sc	5	4.92 ± 0.03	0.61	1.60				
Se	0.193 ± 0.0028	0.16 ± 0.05	31.25	17.10				
Sm					12 ± 0.9	11.4 ± 0.5	4.02	4.75
Tb					1.38	1.5 ± 0.1	4.11	5.80
Th	5.8	5.5 ± 0.3	5.11	5.52	27 ± 5	33.1 ± 1.7	5.07	22.70
U	2	1.8 ± 0.1	6.82	12	7.6	9.7 ± 0.5	5.35	27.89
Yb					4.2 ± 0.8	4.5 ± 0.3	6.65	7.38
Zn	48.9 ± 1.6	39.7 ± 1.8	4.59	18.88	223 ± 19	279 ± 10	3.58	25.5

Table 3: Element concentrations obtained in μg g^{-1}, except where indicated %, in the analysis and uncertainties

	As	1σ	Ba	1σ	Br	1σ	Ca(%)	1σ	Ce	1σ	Co	1σ	Cr	1σ
IN1	7.3	0.7	357	20	95.7	0.6	0.44	0.06	63	3	8.7	0.7	51	3
IN2	5.5	0.6	212	13	66.3	0.4	0.32	0.05	39	2	5.4	0.4	32	2
IN3	12	1	432	24	170	1	0.61	0.09	76	4	10.1	0.7	62	4
IN4	9.6	0.4	334.7	88.4	97.6	0.6	0.36	0.03	53.3	1.7	8.1	0.1	51.9	1.3
IN5	7.8	0.4	338	90	92.1	0.6	0.32	0.03	49.8	1.6	7.8	0.1	49.1	1.3
MAT1	10	1	297	19	88.1	0.5	0.52	0.07	56	3	8	7	50.1	1.3
MAT2	7.6	0.4	427.2	113.4	136.3	0.8	0.40	0.04	48.7	1.6	7.5	0.1	50.1	1.4
MAT3	7.1	0.3	362.9	96.4	127.1	0.6	0.36	0.04	52.2	1.7	7.99	0.08	50.7	1.4
UCC	1.5		550		2.1		3		64		10		35	
	Cs	**1σ**	**Eu**	**1σ**	**Fe(%)**	**1σ**	**Hf**	**1σ**	**K(%)**	**1σ**	**La**	**1σ**	**Lu**	**1σ**
IN1	4.2	0.2	1.1	0.1	3.05	0.03	4.5	0.1	ND		31	1	0.27	0.02
IN2	2.8	0.2	0.75	0.072	1.85	0.02	2.7	0.1	ND		19.8	0.9	0.16	0.01
IN3	4.8	0.3	1.4	0.1	3.54	0.03	4.4	0.1	ND		37	2	0.29	0.02
IN4	3.8	0.8	0.96	0.02	2.63	0.02	2.23	0.03	ND		26.96	0.48	0.26	0.01
IN5	3.3	0.7	0.90	0.02	2.52	0.02	3.41	0.05	0.70	0.29	24.6	0.4	0.22	0.01
MAT1	3.6	0.2	1.1	0.1	3.06	0.03	3.9	0.1	ND		30	1	0.23	0.01
MAT2	3.6	0.2	0.89	0.02	2.56	0.02	3.26	0.05	1.09	0.42	24.96	0.45	0.22	0.01
MAT3	3.6	0.2	0.89	0.02	2.68	0.02	3.23	0.05	0.77	0.25	22.91	0.40	0.21	0.01
UCC	3.7		0.88		3.5		5.8		2.8		30		0.38	

Table 3: continuation

	Na	1σ	Nd	1σ	Rb	1σ	Sb	1σ	Sc	1σ	Se	1σ	Sm	1σ
IN1	1.52	0.04	22	3	67	3	0.40	0.07	11.8	0.5	1.6	0.5	4.9	0.3
IN2	1.07	0.03	17	3	44	2	0.41	0.06	7.4	0.3	1.2	0.4	3.1	0.2
IN3	2.4	0.1	31	5	82	4	0.8	0.1	13.5	0.6	ND		5.9	0.3
IN4	1.66	0.03	30.98	2.71	58.8	2.1	1.01	0.04	8.90	0.04	0.17	0.04	4.3	0.1
IN5	1.57	0.03	23.31	2.35	13.3	0.9	1.1	0.1	8.53	0.04	ND		3.9	0.2
MAT1	1.45	0.04	28	4	64	3	0.6	0.1	10.6	0.4	1.9	0.3	5.0	0.3
MAT2	2.68	0.05	23.7	2.2	56.3	2.3	ND		8.44	0.04	ND		3.8	0.1
MAT3	2.13	0.04	22.2	1.8	63.6	2.5	0.9	0.1	8.88	0.04	0.13	0.05	3.6	0.1
UCC	2.89		26		110		0.2		14		0.05		4.5	
	Ta	**1σ**	**Tb**	**1σ**	**Th**	**1σ**	**U**	**1σ**	**Yb**	**1σ**	**Zn**	**1σ**	**Zr**	**1σ**
IN1	0.78	0.06	0.60	0.09	8.4	0.8	2.4	0.2	1.5	0.2	82	3	208	19
IN2	0.53	0.04	0.30	0.03	5.1	0.5	1.6	0.1	1.0	0.1	37	2	ND	ND
IN3	0.8	0.1	0.56	0.09	9.7	1.0	3.4	0.2	1.7	0.2	92	4	216	26
IN4	0.55	0.03	0.63	0.02	8.3	0.4	2.5	0.1	1.6	0.1	91.5	3.2	170.6	9.2
IN5	0.46	0.04	0.42	0.04	7.6	0.4	2.8	0.1	1.2	0.1	153.6	5.7	99.7	17.3
MAT1	0.74	0.05	0.47	0.06	7.5	0.7	3.4	0.2	1.3	0.2	74	3	192	17
MAT2	0.54	0.05	0.48	0.04	7.3	0.4	2.3	0.1	1.3	0.3	86.6	3.3	132.4	24.9
MAT3	0.61	0.05	0.43	0.04	7.5	0.4	2.4	0.1	1.3	0.1	94.6	3.6	141.9	18.2
UCC	2.2		0.64		11		2.8		2.2		71		190	

The studies of toxic elements in the clay used for human healing [13] have showed results that, when compared with those obtained in this study, indicate that, in general, the concentrations of Co, Cr, La, and Rb are slightly higher, while As, Ba, Br and Zn are slightly lower than the concentrations found in black mud. The concentrations of the elements Ce, Cs, Eu, Hf, Lu, Nd, Sb, Sc, Se, Sm, Ta, Tb, U, Th, Yb and Zr are almost the same in both types of clay.

The Br concentration in *in-natura* and maturated mud varied from 66 to 70 µg g^{-1} and 81.1 to 136.51 µg g^{-1}, respectively, which is a value extremely large when compared with the UCC, with only 2.1 µg g^{-1} [12] and compared with the smectite samples used in pharmaceuticals and cosmetics in Brazil, which vary from 0.5 to 3.3 µg g^{-1} [14]. However, according to the literature, bromine only causes damage in people when inhaled or ingested [11-15], then, the high concentration of bromine should not be a concern.

The study of Rare Earth is important in the interpretation of various geochemical processes and it may be used in the risk assessment of environmental contamination by human activity. The rare earth elements are generally divided into two groups: "light" rare earth, which is represented by La, Ce, Nd, Sm, and Eu, and "heavy" rare earth that includes Tb, Yb and Lu. The results obtained show that the light rare earth varies from 0.75 to 76 µg g^{-1} in *in-natura* mud, while the heavy rare earth varies from 0.16 to 1.70 µg g^{-1}. In the maturated mud, there is ,practically, no difference when compared with *in-natura* mud, in which the concentrations of light rare earths varied from 0.59 to 56 µg g^{-1} and in the heavy rare earths varied from 0.21 to 1.34 µg g^{-1}.

Comparing the five *in-natura* and three maturated types of mud with UCC is possible to notice that the rare earth elements are, practically, in the same order of concentration and the variations are, also, almost the same, from 0.88 to 64 µg g^{-1} for light rare earth and 0.38 to 2.20 µg g^{-1} for heavy rare earth elements[12]. In this study, a simple normalization comparing the results with values obtained from UCC was applied [12] and the results are shown in Figure 1. It is possible to observe in this figure that Ca, Rb and Ta are highly depleted, while As, Se and Sb are highly enriched, when compared with UCC values. The other elements follow almost the same order of magnitude, for both *in-natura* and maturated types of mud. Only in samples IN4 and MAT2, smaller values for Se were found.

A more complex approach for normalization of geochemical data to a reference metal, more frequently used in investigations of contaminated sediments, is the Enrichment Factor (EF). The assumption is that the reference metal used represents a certain mineral fraction of the sediment. The reference metal should, therefore, be an important constituent of one or more of the major fine-grained trace metal carrier(s) and reflects their granular variability in the sediment. The most frequently used reference metal is Al, which represents a chemical tracer of Al-silicates, particularly, the clay minerals. Some other non-anthropogenic elements such as Sc, Cs, Rb and Co can also be used instead. A simple approach to the normalization of geochemical data is to compare the total metal concentrations of surface sediments with concentrations characteristic of natural background levels or uncontaminated sediments [8]. This procedure is applied to know which elements are enriched. In this study, Sc was utilized in the analysis and the results are shown in figure 2.

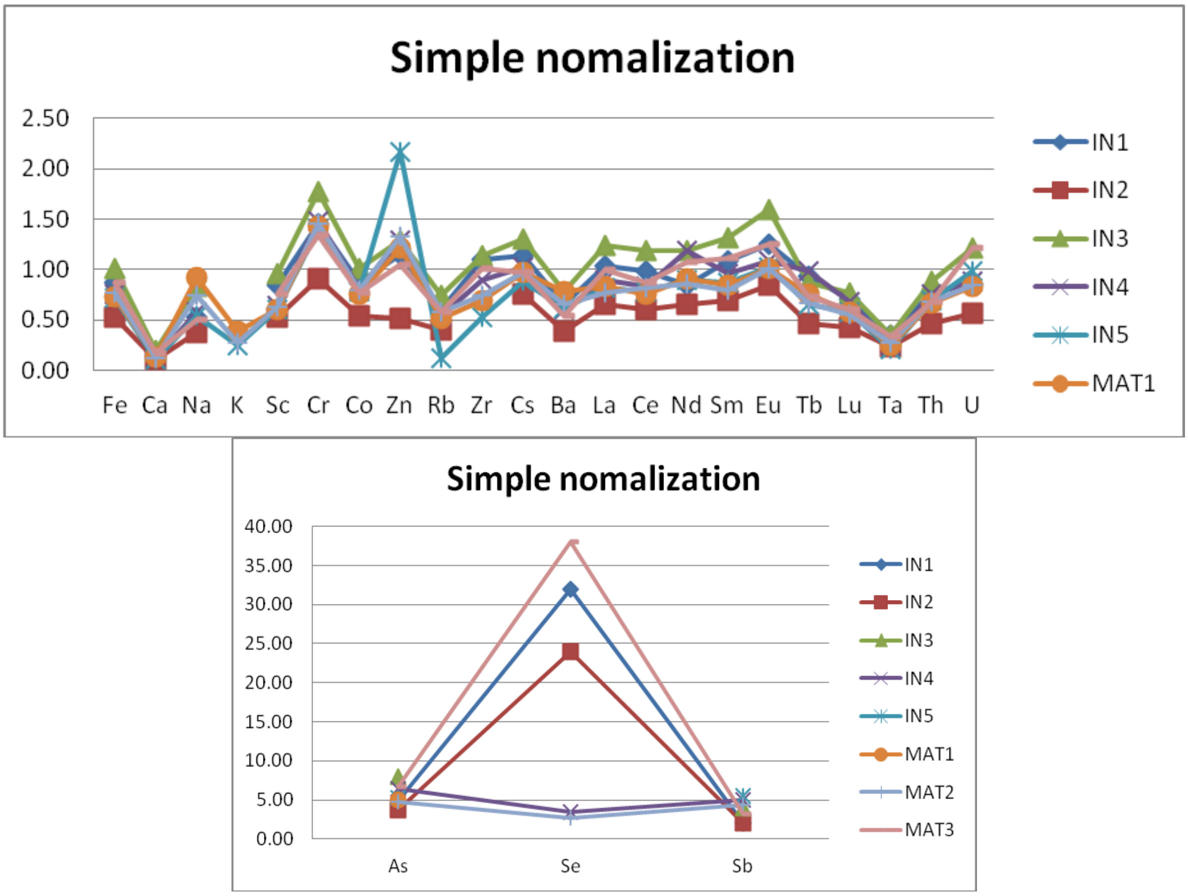

Figure 1: Simple normalization in *in-natura* (IN) 1, 2, 3, 4 and 5 and in maturated (MAT) 1, 2 and 3.

It was verified that As, Br, Ce, Co, Cr, Cs, Eu, Fe, La, Nd, Sb, Sc, Se, Sm, Tb, U, Zn and Zr are enriched. Emphasis to As, Br, Se and Sb, which are much more enriched than the others, while Ba, Ca, Hf, K, Lu, Na, Rb, Ta, Th and Yb are depleted.

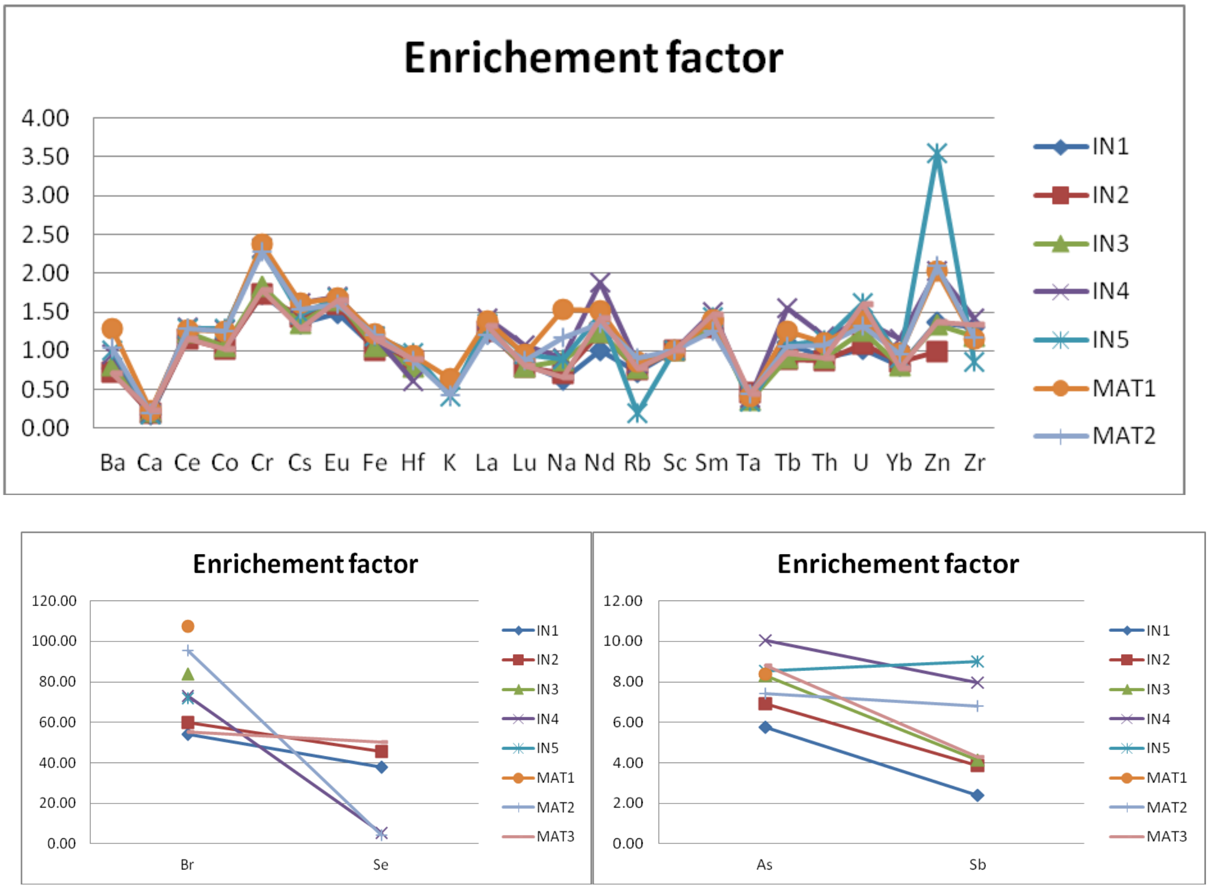

Figure 2: Enrichement factor in *in-natura* (IN) 1, 2, 3, 4 and 5 and in maturated (MAT) 1, 2 and 3.

4. CONCLUSIONS

Five *in natura* and three maturated Black Mud samples were collected in Peruíbe city, located in the south of São Paulo State, Brazil. The mud samples were analyzed for the determination of moisture, organic matter and loss on ignition; element concentrations were verified by neutron activation analysis. The results indicated that the Peruíbe black mud is enriched with organic matter. Higher concentrations were found to the elements As, Ba, Br and Zn, while smaller concentrations for the elements Co, Cr, La, and Rb were verified, when compared to other medicinal types of mud.

In comparison with the upper continental crust, the elements Ca, Rb and Ta are highly depleted, while As, Se and Sb are highly enriched. Enrichment factors, also, showed high values for the same elements, besides Br. Given the use of Peruíbe Black Mud for medicinal purposes, future studies may indicate if the elements here identified may exert some therapeutic influence in healing processes.

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