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Evaluation of the presence of radionuclides of natural origin (NORM) and rare earths in the Brazilian Red Mud

ABSTRACT

- The aim of this study is the chemical and mineralogical characterization of Brazilian red mud from the States of Pará and São Paulo, as well as the determination of the specific activities of naturally occurring radionuclides (NORMs) and the presence of rare earth elements (REE);

- The evaluation of radionuclides was carried out using the gamma spectrometry technique and the quantification of the REE was performed using the ICP-AES and ICP-MS techniques;

- With the ICP-MS technique, the total REE was 841,20 ppm and a total of 752,06 ppm for the ICP-AES technique. These results demonstrate that this residue has potential for the use of these elements;

- In the evaluation of NORMs, values of U-238,Th-232 and K-40 were found below the values recommended by the IAEA, making this residue can be reused in the civil construction and ceramic industries. Samples from Pará showed higher values than samples from São Paulo.

INTRODUCTION

All minerals and raw materials contain radionuclides of natural origin, of which the most important for radiological protection purposes are the radionuclides of the decay series of Uranium-238 and Thorium-232 and Potassium-40.

Mining industries have been considered one of the largest sources of waste production and can be classified as potentially generating NORMs. Depending on the radioactivity levels, they may require occupational and environmental radiological control appropriate to their characteristics, but little concern has been given to the existence of natural radionuclides.

Currently, mining residues have been studied and considered one of the secondary sources for the use of REE. Red mud is an insoluble residue, very rich in aluminum, iron, silicon and rare earths. The disposal of this waste represents the biggest environmental problem for the Bauxite processing industries.

In this way, analyzing the activity of NORMs and quantifying the REE, present in the red sludge, will allow to estimate the exposure of workers and the public around the industry, and will also contribute with information on the use and applicability of this residue in the cement, ceramic and reuse sector REE, thus minimizing environmental impacts.

METHODOLOGY

The Brazilian red mud samples were supplied by bauxite refining industries located in the State of Pará and in the State of São Paulo.

Characterization of the sample:

* SEM;

* XRD.

Determination of U, Th and K activity (NORM):

* Calculation of the estimated absorbed dose and equivalent of gamma radiation and the gamma activity concentration index;

* Assessment of the potential for exposure that new materials produced with this waste may cause.

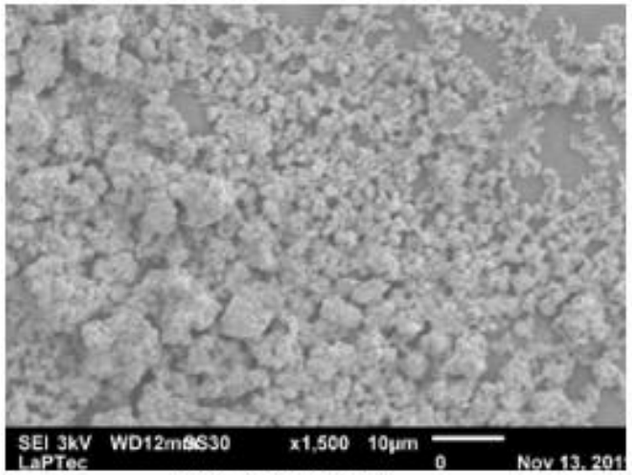
Quantification of REE presence:

* Comparison between ICP-MS and ICP-AES techniques;

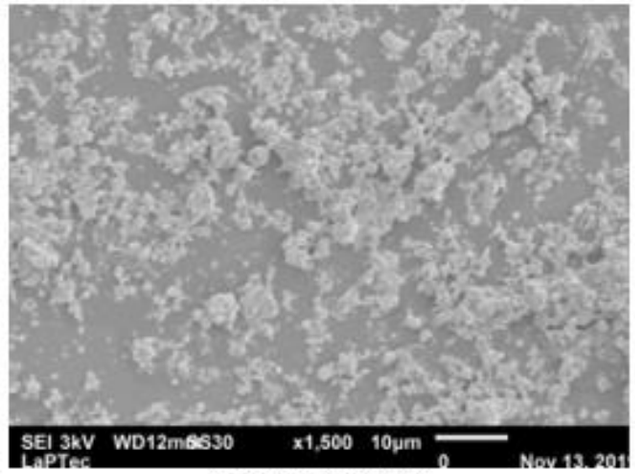
* Assessment of the potential for using red mud for rare earths.

RESULTS

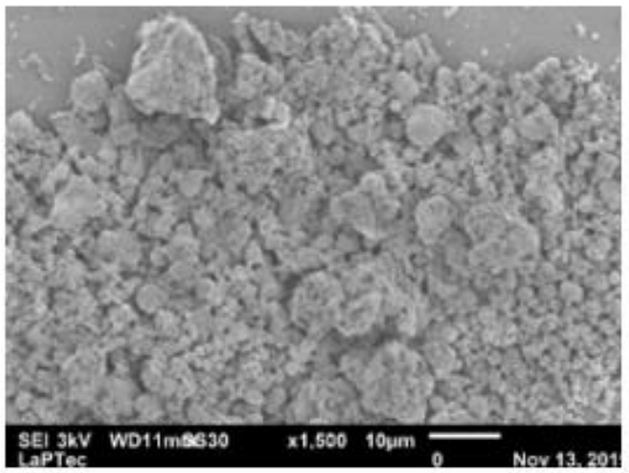
Characterization by SEM



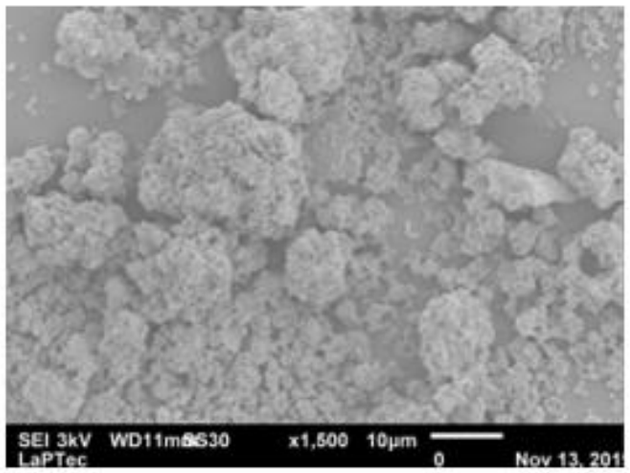
(A)-LVS2015



(B)-LVS2000



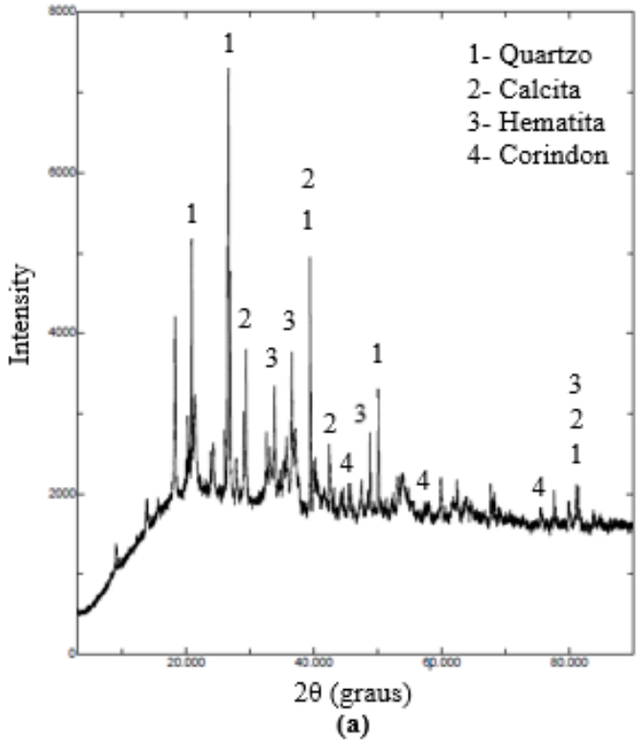
(C)-LVP2019

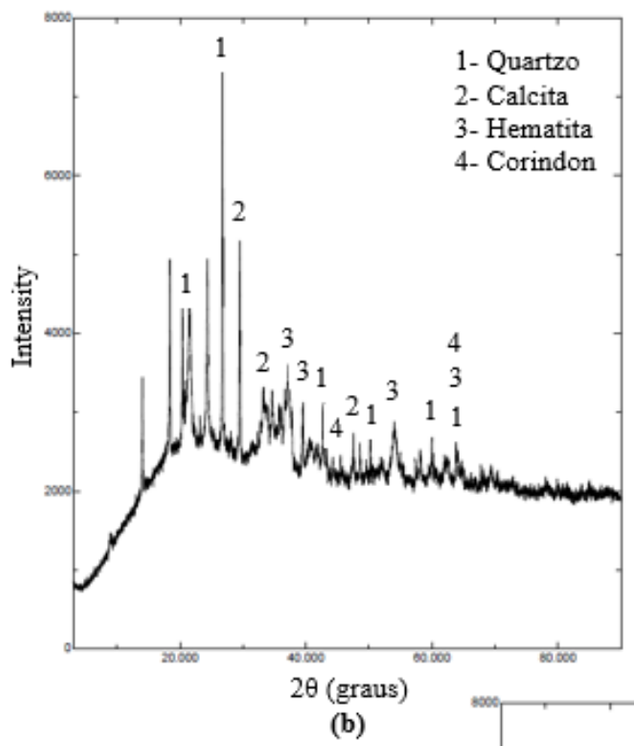


(D)-LVP2017

Samples	Chemical composition (%)				
	Al_2O_3	Fe_2O_3	$CaCO_3$	SiO_2	Total
LVS2011	17,00	21,00	35,00	27,00	100,00
LVS2015	18,00	20,00	36,00	26,00	100,00
LVP2017	24,00	58,00	13,00	5,00	100,00
LVP2019	18,00	64,00	12,00	6,00	100,00

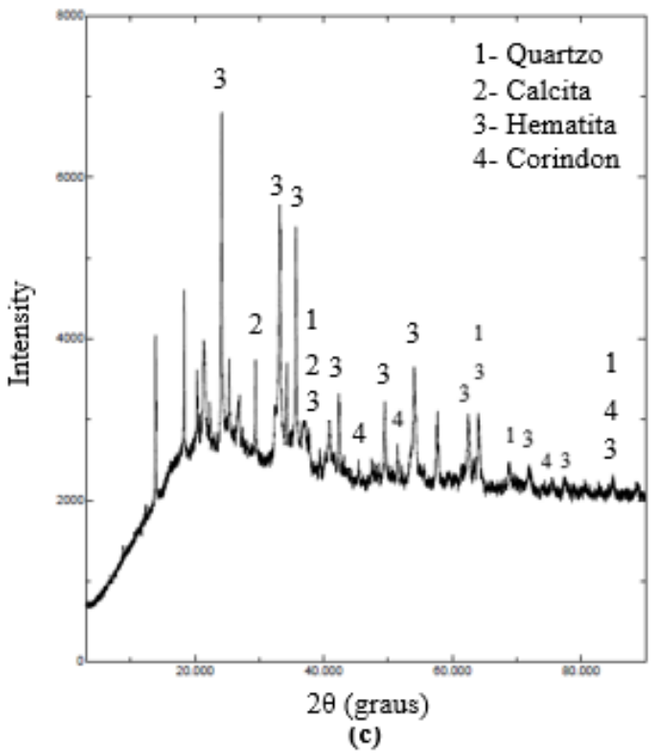
Characterization by XRD

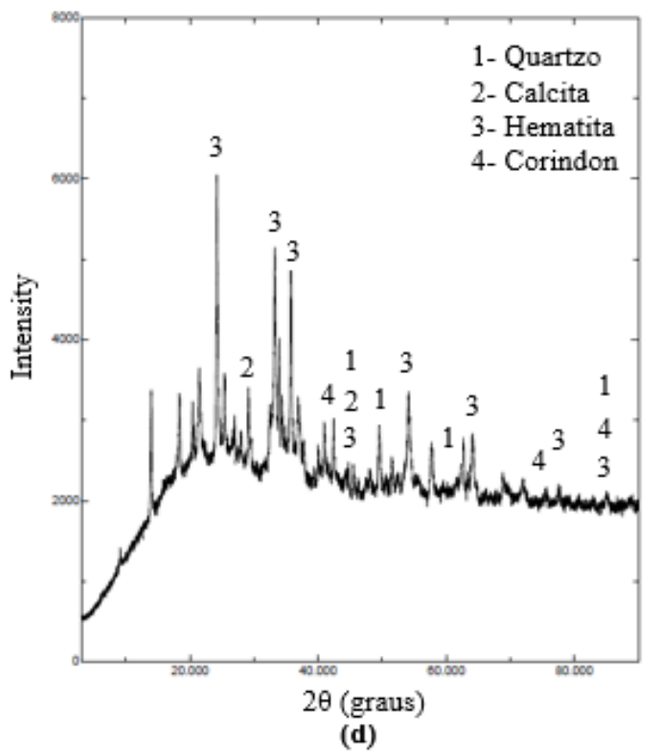




The samples from the state of Pará (c and d) have higher hematite peaks compared to the samples from the state of São Paulo (a and b).

In relation to quartz ore, it is found in greater abundance in samples from the state of São Paulo than from the state of Pará.





Determination of U, Th and K activity (NORM)

Samples	^{238}U (Bq/kg)	^{232}Th (Bq/kg)	^{40}K (Bq/kg)
LVS2015	51,15 ± 6,28	58,30 ± 6,10	47,98 ± 8,40
LVP2019	163,68 ± 17,76	436,58 ± 12,02	52,15 ± 10,59

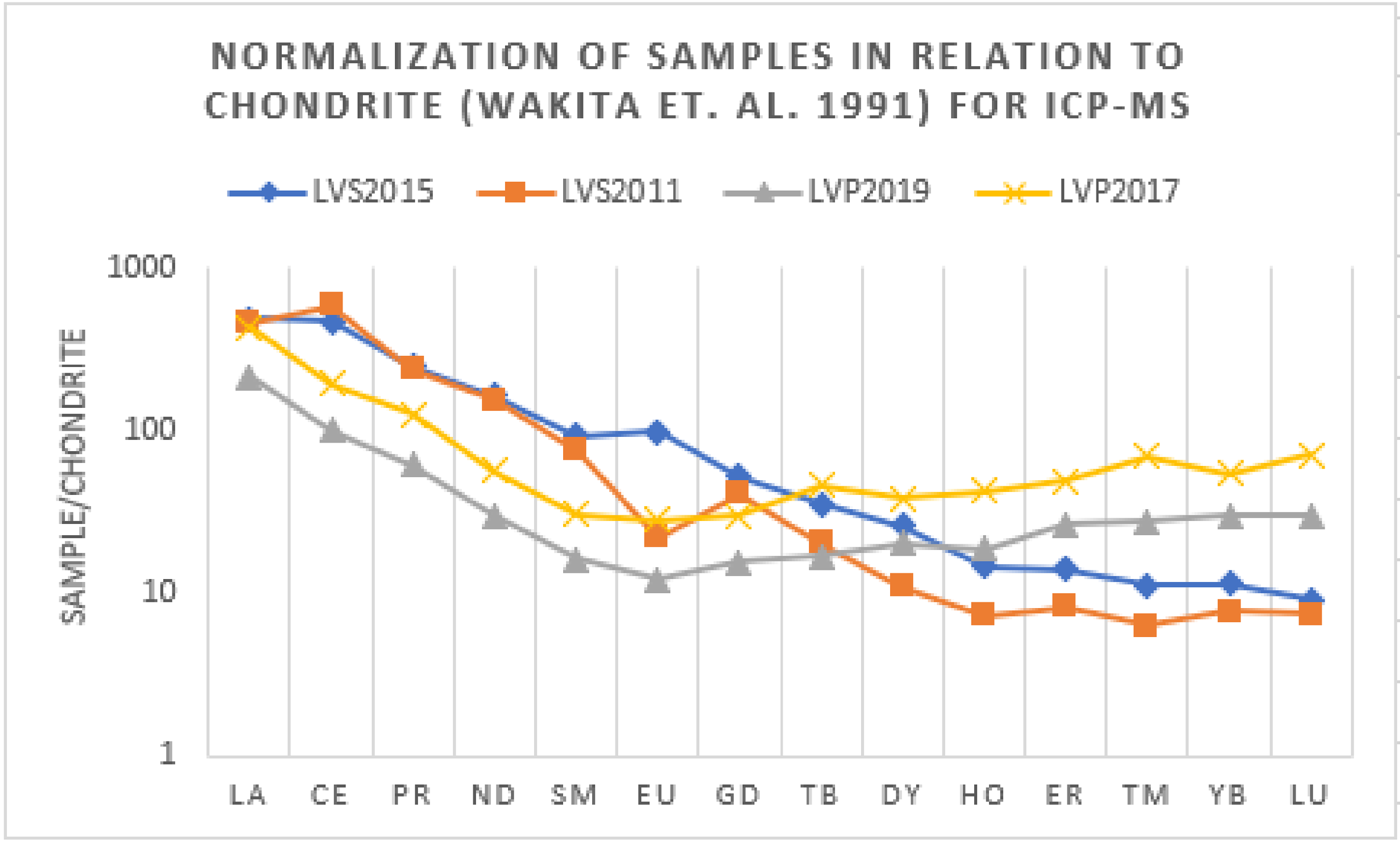
Samples	Absorbed dose (nGy/h)	Effective equivalent dose (µSv/ano)	Gamma activity concentration index
LVS2015	60,81	364,26	0,477
LVP2019	297.02	74,57	2,746
Recommended limits	**55***	**1000**	**1000**
Source	**UNSCEAR, 1993**	**ICRP, 1990**	**ICRP, 1999**

*** Recommended Absorbed Dose Limit for Soil.**

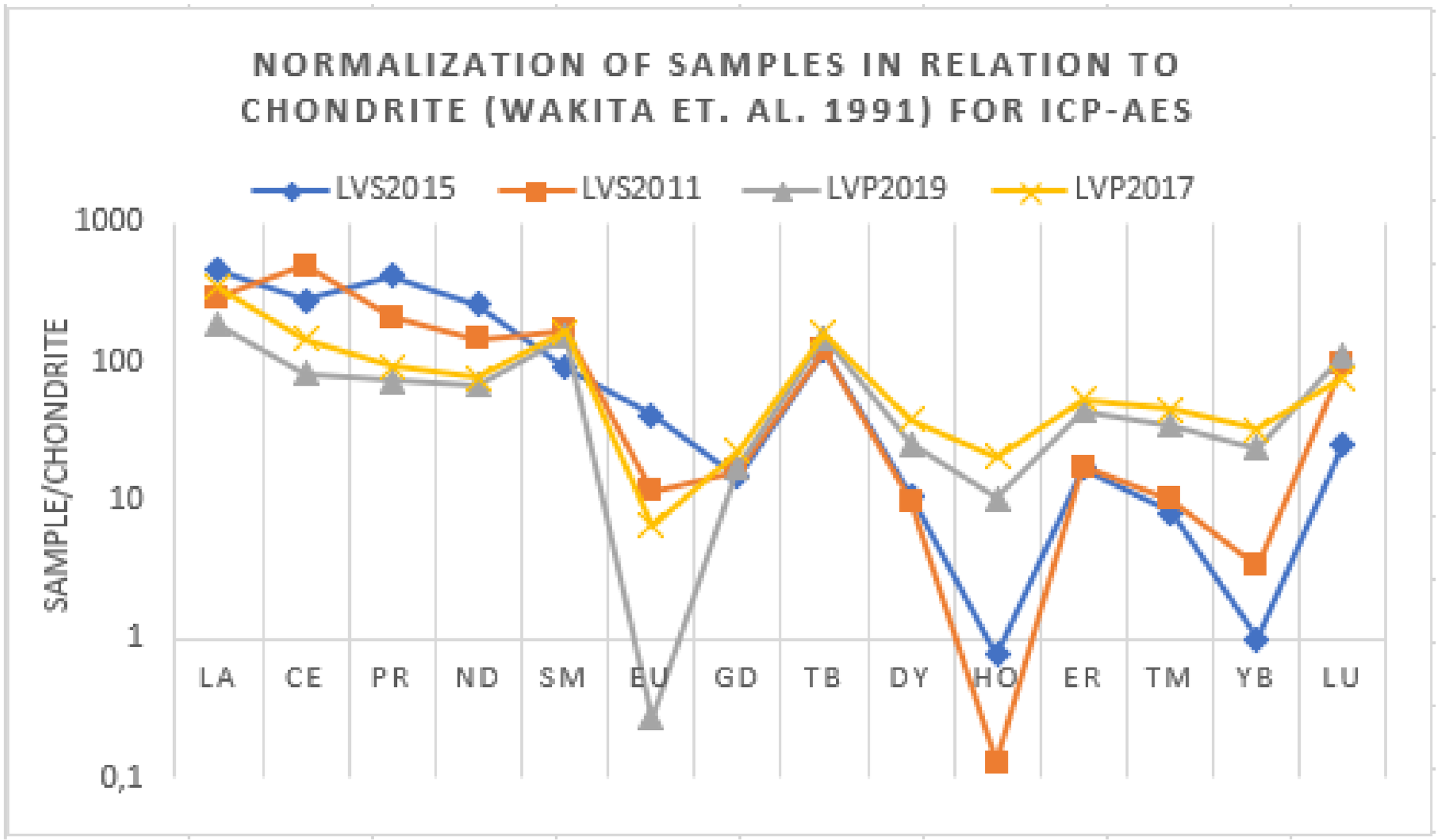
Quantification of rare earth elements in red mud

REE	ICP-MS				ICP-AES			
	LVS2015 (ppm)	LVS2011 (ppm)	LVP2019 (ppm)	LVP2017 (ppm)	LVS2015 (ppm)	LVS2011 (ppm)	LVP2019 (ppm)	LVP2017 (ppm)
Sc	72,15	41,52	21,84	35,10	57,40	28,38	15,29	19,38
Y	19,79	12,39	37,94	68,41	3,63	4,26	28,32	46,39
La	142,53	165,40	70,80	129,58	156,00	99,56	62,06	116,39
Ce	390,50	451,27	88,69	145,53	249,69	447,08	74,95	130,96
Pr	28,18	27,90	7,83	18,26	50,00	25,39	8,77	11,30
Nd	132,69	108,68	17,93	35,29	163,43	93,02	43,30	49,11
Sm	14,37	13,30	2,80	5,30	17,45	32,78	29,99	31,93
Eu	6,82	1,84	0,78	2,43	3,02	0,86	0,02	0,48
Gd	11,99	10,54	4,36	6,89	3,85	4,26	4,50	5,90
Tb	1,42	0,87	0,77	2,32	5,72	5,67	7,03	7,45
Dy	7,81	2,86	5,81	9,65	3,29	2,93	7,69	11,45
Ho	0,98	0,67	1,71	3,46	0,06	0,01	0,80	1,63
Er	2,67	1,71	4,61	11,33	3,41	3,52	8,94	10,74
Tm	0,36	0,31	1,11	2,72	0,26	0,32	1,11	1,44
Yb	2,72	1,63	6,14	10,12	0,22	0,75	5,22	7,17
Lu	0,29	0,31	1,35	2,75	0,86	3,27	3,82	2,58
Total	835,27	841,20	274,47	489,14	718,29	752,06	301,81	454,30

Quantification of rare earth elements in red mud



Quantification of rare earth elements in red mud



DISCUSSION

Characterization by SEM

- The sludge samples are constituted by particles of granular variety and heterogeneity, containing particles from values larger than 10 μm to particles with fractions smaller than 1 μm;
- Comparing the micrographs of the São Paulo State red sludge (A and B) with the Pará State red sludge (C and D), it is notable that the São Paulo State sludge grains are smaller (<5 μm) in relation to mud from the State of Pará, which have larger particles (>10 μm), both without any regular pattern;
- As for the chemical composition, both have the same chemical composition and the same elements. The red mud samples from the State of Pará have higher iron oxide values than the red mud samples from the State of São Paulo, which makes them more reddish than those from the State of São Paulo;

Determination of U, Th and K activity (NORM)

- Depending on the NORMs values, there is a very high discrepancy in the activity values of the red mud samples generated in the state of Pará, for Th-232, in relation to the samples generated in the state of São Paulo, almost ten times higher and for U-238, almost 3 times higher. This may be due to the geology of the regions where the original bauxite is obtained and needs to be further investigated. In relation to K-40, the values for the two samples remained practically the same;
- According to the BSS (2014), materials containing U-238, Th-232 concentrations below 1 kBq/kg and K-40 concentrations below 10 kBq/kg are exempt from any radiological characterization, as they are unlikely to cause an increase in radiological exposure;
- By calculating the Absorbed Dose, Effective Equivalent Dose and the gamma activity concentration index, both samples were below the internationally recommended limits by UNSCEAR and ICRP. In this way, the red mud from the states of Pará and São Paulo can be considered of low radiological exposure and be reused for the civil construction industries, not presenting risks to the general population and workers.

Quantification of rare earth elements in red mud

- Red mud samples show variable REE contents with ∑REE (including Sc and Y) in the range of 274,47 to 841,20 ppm. Light REE (LREE) are relatively more enriched compared to heavy REE (HREE) for all samples, with ∑LREE ranging from 193,19 – 748,93 ppm, and an ∑HREE ranging from 8,36 – 115,72 ppm;
- The samples show negative anomalies in some of the REE, such as La, Pr, Sm, Eu, Tb, Ho, Tm and Lu, and positive anomalies for the elements Ce, Nd, Gd, Dy, Er and Yb, for the measurements performed by ICP-MS. Unlike what is observed in the ICP-AES measurements, the samples show negative anomalies in most REEs La, Pr, Sm, Eu, Gb, Tb, Dy, Ho, Tm Yb and Lu, with only the elements Ce, Nd and Er showing positive anomalies;
- For the two analytical methods, ICP-AES and ICP-MS, for which the analytical procedure is similar, ICP-MS is more sensitive for most elements. However, the greatest sensitivity is gained by a higher dilution factor (0.05% sample content in the final solution for the ICP-MS);

Quantification of rare earth elements in red mud

- To estimate the potential of REE in red mud, we considered an average value of 800 ppm of REE and a slurry stock produced and stored from alumina refining in the states of Pará and São Paulo in 2016, 2017 and 2018;
- There are approximately 5403.75 Mt of red mud that are dried and piled up at the CBA company, in the State of São Paulo, while at least 41,124.75 Mt of red mud are contained in the tailings ponds at the Paragominas company, in the State of Pará , with waste being produced throughout the year;
- These data demonstrate that there is a potential for red sludge to make a substantial contribution to the supply of REE, as REE reserves in Brazil are estimated at 21 Mt, and production in the last two years, 2019 and 2020, was 710 Mt and 1000 Mt, respectively.

CONCLUSIONS

- With the determination of radionuclides of natural origin (NORMs) it was possible to understand that from the point of view of Radiological Protection, red mud samples have low gamma radiation dose values and human exposure, so they can be used for the various types of construction materials, but it is important to bear in mind that the total exposure due to the sum of the contribution of each material can bring some risks.

- From the quantification of rare earth elements by ICP-OES and ICP-MS techniques, we were able to estimate the potential of REE in Brazilian muds. Sludges can represent a potential REE resource, but it will also and essentially depend on the extraction techniques to be used. This, in turn, will allow a clear economic quantification of the potential resources of these elements in Brazilian red mud.

THANK YOU FOR YOUR ATTENTION