



Element Concentrations in Niobium Tailing Carbonate, Soil and Lettuce by Instrumental Neutron Activation Analysis and X-ray Diffraction

R. M. Ayllon¹, J. K. Torrecilha¹, H. M.
S. M. D. Linhares², T. M. El Hajj³, M. R.
Furlan⁴ and P. S. C. Silva¹

¹ *rafaellayllon@gmail.com,*
jeffkoy@hotmail.com, pscsilva@ipen.br
Instituto de Pesquisas Energéticas e Nucleares
(IPEN / CNEN - SP) Av. Professor Lineu
Prestes 2242. 05508-000 São Paulo, SP
² *horaciolinhaires@id.uff.br, Instituto do*
Noroeste Fluminense de Educação Superior
(UFF - RJ), Avenida João Jasbick, s/nº, 2847-
0000 - Santo Antônio de Pádua, RJ
³ *thammiris.hajj@unifal-mg.edu.br,*
Universidade Federal de Alfenas (UNIFAL-
MG), Rodovia José Aurélio Vilela, 11999,
Poços de Caldas, MG
⁴ *furlanagro@gmail.com, Universidade de*
Taubaté (UNITAU – SP), Rua Quatro de
março, 432, 12020-270, São Paulo, SP, Brasil

1. Introduction

Brazil is rich in mineral resources and mining is important for economic infrastructure, as it creates jobs, improves technologies and improves quality of life. However, it is important to recognize the impacts associated with this activity, especially in the generation of waste and rejects. Furthermore, there are concerns about exploitation in sensitive areas, such as forests and indigenous lands, leading to debates about the need to reconcile economic development with environmental preservation and the rights of local communities. It is important that policies and regulations associated with mining are effective, promoting sustainable practices and mitigating environmental impacts.

A possible use of mining residues with the aim of mitigating socio-environmental problems would be to use them as soil conditioners. A first benefit is the reduction of the toxicity of some chemical elements and consequently an increase in the availability of other elements considered micronutrients for plants [1]. This paper aims to evaluate the distribution of elements As, Ba, Ca, Ce, Eu, Fe, K, La, Lu, Mg, Mn, Nd, Sc, Sm, Ta, Tb, Zn, Zr and Yb content in a carbonate niobium residue.

2. Methodology

Sampling

The carbonate samples were supplied by a NORM industry, located in Catalão, Goiás, Brazil. The soil for lettuce (*Lactuca sativa L.*) plantation was collected in Taubate, São Paulo, Brazil. A portion of this soil was separated for analysis before the plantation and a second analysis was made after plantation.

The planting and care of the lettuce samples were made at the University of Taubate on the Agronomy campus using completely randomized design (CRD) model, in a 4x5 factorial scheme: soil and limestone; soil and carbonate; and, control soil, in five repetitions [2]. In each crop it was used the proportion of 1 kg of soil for 3g of the amendment [3, 4]. Two plantings were conducted in the same pots without soil reposition [5]. For analysis, the carbonate and soil samples were air dried and non-soil material were removed. Samples were then dried at 100 °C for 24 h, crushed and homogenized by passing it through a 125- μ m sieve. Lettuce samples were weighed and calcinated at 1000°C for 1h. For sample irradiation, 120 mg was used in duplicate.

Instrumental Neutron Activation Analysis

For INAA, samples, reference materials, and synthetic standards were packed in plastic bags, placed in aluminum capsules, sealed and sent to irradiation for periods of 8 hours in the IEA-R1 nuclear reactor. Gamma spectrometry was carried out after seven days and after 15 days of decay. The measurements were done using a HPGe detector, EG&G Ortec with a resolution of 0.88 keV and 1.90 keV for the 122 keV and 1332 keV peaks of ^{57}Co and ^{60}Co , respectively. As reference materials Estuarine Sediment, SRM 1646a from the National Institute of Standards and technology (NIST), and Syenite Table Mountain e STM-2 from the United States Geological Survey (USGS)) were used.

Mineralogical characterization of niobium mining exclusion

The mineralogical analysis of the carbonate samples (n=6) was carried out using X-ray Diffraction (XRD) for the identification of the minerals present [6]. The diffractograms were obtained using SmartLab SE equipment, Rigaku brand, operating with a copper tube (wavelength $k_{\alpha 1}=1.54059\text{\AA}$), linear detector Dtex Ultra 250.

3. Results and Discussion

Figure 1 shows the results obtained using the X-ray diffraction technique showing the presence of biotite, calcite, richterite, dolomite and fluorapatite. All samples presented the same diffraction peaks, indicating homogeneity of the samples in relation to the mineral phases.

Table 1 shows the element concentrations and the sum of the REE concentrations (Ce, Eu, La, Lu, Nd, Sc, Sm, Tb and Yb). The concentration of Ba in carbonate is higher than in the analyzed soil, causing an increase in the concentration of the mixture conditioned with it and in the lettuce plants of this treatment. However, this element has a concentration below the world average (362 – 580 mg kg⁻¹) and is not essential to plant tissue [7].

In the control soil and carbonate, Mg exhibited elevated concentrations, resulting in lettuce grown in in this treatment higher in the second harvesting. In the carbonate, As levels were below the detection limit. Given its toxicity to humans, the permissible value for As in contaminated soil is 2000 mg kg⁻¹ that is higher than the value found in the control soil [7].

Zr tends to accumulate more in legumes and trees than in other plant species. In this study, Zr concentration values in lettuce were found to be higher during the second planting than the first, surpassing reference values 0.41 - 0.62 mg kg⁻¹ [7]. The concentration of Ta in the control soil aligns with global soil standards (1.1 mg kg⁻¹), but when the soil is conditioned, the carbonate treatment exhibits a concentration higher than the global average. Nevertheless, the lettuces analyzed adhere to the permissible global value (< 1 µm kg⁻¹) [7].

The presence of rare earth elements (REE) in the soil can also improve the production, quality of plantations and pest control, with their benefits being observed at different stages of plant growth. However, their possible health risks are not known [8]. The REE in the soil can alter the availability of some nutrients for plants, for example the absorption of Ca, Na, Zn and Mn by the plant can be decreased if the soil has a high concentration of La and Ce. In general, the Brazil soils presents REE concentrations higher than UCC [7, 9, 10].

The amendment with carbonate contributed to the enrichment of Ca in the soil, due to the presence of minerals such as calcite, dolomite and fluorapatite. The presence of Ca in soils increases two important factors in agriculture: pH and exchangeable base levels, which favors plant growth [1, 3].

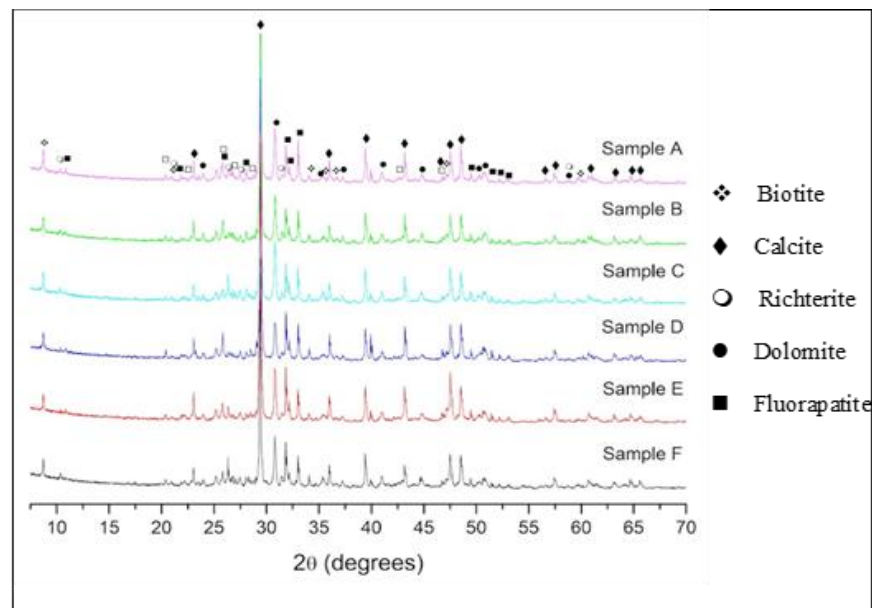


Figure 1 Diffractograms obtained for the carbonate samples analyzed in this study

Table 1 Concentration, in mg kg⁻¹ or percentage, for carbonate, soil (S) and lettuce (L) samples obtained by INAA.

Correção do texto

Samples	As	Ba	Ca [%]	Fe [%]	K [%]	Mg
Carbonate	-	30403 ± 1594	37.4 ± 0.4	4.44 ± 0.05	1.6 ± 0.1	1379 ± 198
S. Control	4.6 ± 0.1	282 ± 13	0.86 ± 0.04	2.62 ± 0.02	1.03 ± 0.04	5759 ± 393
S. Carbonate	5.1 ± 0.1	1049 ± 25	1.17 ± 0.03	3.34 ± 0.02	0.80 ± 0.03	988 ± 52
S. Lime	7.3 ± 0.1	229 ± 13	0.97 ± 0.03	3.72 ± 0.02	0.58 ± 0.04	1594 ± 247
L.Control ^a	0.003 ± 0.001	0.47 ± 0.04	0.06 ± 0.01	0.000398 ± 0.000003	1.18 ± 0.02	32 ± 2
L. Carbonate ^a	0.0008 ± 0.0001	3.18 ± 0.09	0.108 ± 0.001	0.00255 ± 0.00001	1.35 ± 0.02	43 ± 2
L. Lime ^a	0.008 ± 0.001	2.9 ± 0.1	0.093 ± 0.002	0.00386 ± 0.00002	2.22 ± 0.05	45 ± 4
L. control ^b	-	1.0 ± 0.1	0.407 ± 0.011	0.00072 ± 0.00001	2.39 ± 0.04	141 ± 4
L. Carbonate ^b	-	10.2 ± 0.3	0.314 ± 0.007	0.00532 ± 0.00003	2.16 ± 0.03	102 ± 5
L. Lime ^b	0.0035 ± 0.0009	6.1 ± 0.3	0.266 ± 0.004	0.00686 ± 0.00003	1.73 ± 0.02	75 ± 3

Samples	Mn	Ta	Zn	Zr	REE sum [Ce, Eu, La, Lu, Nd, Sc, Sm, Tb, Yb]
Carbonate	3864 ± 25	1.8 ± 0.1	-	3021 ± 84	10251
S. Control	794 ± 5	1.10 ± 0.04	66 ± 2	739 ± 20	345
S. Carbonate	631 ± 3	1.75 ± 0.04	84 ± 2	926 ± 11	496
S. Lime	600 ± 4	1.65 ± 0.03	51 ± 1	798 ± 14	255
L.Control ^a	13.11 ± 0.05	0.00006 ± 0.00002	4.19 ± 0.07	0.49 ± 0.06	0.14
L. Carbonate ^a	13.72 ± 0.07	0.00023 ± 0.00007	7.70 ± 0.08	0.10 ± 0.01	0.23
L. Lime ^a	26 ± 4	0.0018 ± 0.0001	4.44 ± 0.06	0.39 ± 0.06	0.27
L. control ^b	44.8 ± 0.2	-	3.25 ± 0.03	-	0.04
L. Carbonate ^b	46 ± 2	0.0006 ± 0.0001	10.8 ± 0.1	0.8 ± 0.2	0.45
L. Lime ^b	16.32 ± 0.08	0.0014 ± 0.0002	11.8 ± 0.1	1.0 ± 0.1	0.99

^aFirst crop; ^b second crop

S. Soil; L. Lettuce

4. Conclusions

This study evaluated the possibility of using a carbonate niobium residue as agricultural amendment, whose mineralogical composition include biotite, calcite, dolomite and fluorapatite. This carbonate is rich in Ca, Ba, Fe, K, Mn, Zr and REE. Carbonate mended soil was increased in the amount of Ba, Ca, Fe and Ta, when compared to control soil and with soil treated with lime.

Lettuce showed an increase in Ba, Ca, Fe, K, Mg, Mn, Zn and Zr in the second crop, for control and carbonate treatments. The toxic element As is below the detection limits in carbonate and it was found in very low concentrations in the plants. The REE were absorbed in higher amounts in lettuce in second crop of carbonate and lime treatment. Barium, a non essential element and possibly toxic to humans presented values relatively high.

By the initial results obtained from carbonate, the application of the mining waste in agriculture present advantages while still needs to be further evaluated.

Acknowledgements

The authors would like to acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the scholarship and financial support (n. 140439/2019-6). Authors are grateful to Mr. Ferreira and CMOC International for authorizing the sampling.

References

- [1] F. N. S. Souza, Oliveira, C. G., Martins, É. S., & Alves, J. M. "Efeitos condicionador e nutricional de um remineralizador de solos obtido de resíduos de mineração", *Agri-Environmental Sciences*, v. 3, n. 1, p. 1-14, (2017).
- [2] J.R. Costa. *Técnicas experimentais aplicadas às ciências agrárias*. Seropédica: Embrapa Agrobiologia, 2003. 102 p. Rio de Janeiro & Brasil (2003).
- [3] J.A. Albuquerque, C. Bayer, P. R. Ernani, E. C. Fontana. "Propriedades físicas e eletroquímicas de um Latossolo Bruno afetadas pela calagem". *Revista Brasileira de Ciência do Solo*, vol. 24, pp. 295-300 (2000).
- [4] W.J. Goedert, D. M. G. de Sousa. *Critérios para recomendação de calagem e adubação*. Planaltina - DF & Brasil (1987).
- [5] T. Aziz, S. Ullah, A. Sattar, M. Nasim, M. Farooq, M. M. Khan. "Nutrient availability and maize (*Zea mays*) growth in soil amended with organic manures". *International Journal of Agriculture and Biology*, v. 12, n. 4, p. 621-624 (2010).
- [6] M. Ermrich, D. Opper. *XRD for the analyst. Getting acquainted with the principles*. Panalytical, Kassel & Germany (2013).
- [7] A. Kabata-Pendias. *Trace elements in soils and plants*. CRC press, Florida & USA (2000).
- [8] J. S. B. Oliveira, V. Biondo, M. F. Saab, K. R. F. Schawn-Estrada. "Uso de elementos Terras Raras na agricultura", *Scientia Agraria Paranaensis*, v. 13, n. 3, p. 171-185 (2014).
- [9] K. H. Wedepohl. "The composition of the continental crust". *Geochimica et cosmochimica Acta*, v. 59, n. 7, p. 1217-1232, (1995).
- [10] D. L. Sparks. "Environmental soil chemistry: An overview". *Environmental soil chemistry*, v. 2, p. 1-42, (2003).