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INCOMPATIBLE ELEMENTS IN BOTTOM SEDIMENTS OF THE ACARAY DAM RESERVOIR

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Abstract. *Incompatible elements (IE) from the bottom sediments of the Acaray Reservoir in the Alto Paraná region of Eastern Paraguay were investigated by the EDXRF technique. Most of them are refractory, that is, they maintain their primary relationships and are transferred almost directly into sediments and thus, they are considered as geoindicators. In this regard, IE are of utmost interest in sediments studies. The refractory trace elements analyzed were Y-Rb-Sr-Zr-Nb-Ba-La-Ce-Nd, and the minor elements Ti-Mn-Fe. The analyses were performed with an Am-241 source and an X-ray tube. Samples were taken from six different stations. Like the sediments of the Itaipu Dam, spidergram results show an enrichment of IE and contributions of sedimentary material to the bottom sediments of the Acaray Reservoir.*

Key words: *Acaray Dam, Itaipú Dam, incompatible elements, bottom sediments, refractory elements, spidergram*

1. INTRODUCTION

The Acaray River originates from several streams in the heights of Aracanguy, San Joaquin in the Caaguazu mountain range. It runs downstream eastward and slightly to the south to its discharge into the Parana River with a length of ~300 km. Its basin is 10,540 km^2 and it traverses areas of the Misiones Formation (MF) [1-3]. The average flow is Q_m=180 m^3/s; the maximum values exceed 500 m^3/s whereas the minimum values are reduced to values lower than 50 m^3/s, evidencing a wide variability of these flows. The longitudinal profile of this river shows steep slopes in the first 15 to 20 km and is then reduced to much lower values until the site of the Acaray Dam, from where this slope is again accentuated.

The drainage density is about 0.23 km/km^2. In the middle and lower sections, the course goes through areas with sedimentary soils with low runoff speed producing numerous meanders, so the deposition of sediments can be expected. Due to the limited conduction capacity of the channel, it is unable to contain the water during the floods, which causes extravasation and the flooding of marginal lands.

Using existing cartography/satellite imagery as well as information from data generated/processed by Hydroconsult and held in its repository, it was possible to establish a preliminary classification of the hydrological characteristics of the soils in the basin. Thus, it can be said that the imbriferous crests of the mountain range are covered by relatively impermeable material up to a height of about 200 or 250 meters that has been classified from the point of view of runoff as type C, with the relatively high power of surface runoff production and a low infiltration capacity. They are relatively poorly permeable soils.

Between the aforementioned level and the height of 100 masl, the soil could be classified as type B, defined by the Soil Conservation Service as moderate permeability soil, which is higher than in the previous case. Finally, below the 100 m elevation, soils have been classified as type A with permeability even higher than those of type B, where there is greater infiltration due to sand and silt.

At about 10 km from its outlet into the Parana, the Acaray Hydropower Dam plant was built. Its Reservoir (AR) is situated in Hernandarias, close to the Itaipu Dam (ID) [1]. The lake covers an area of 20 km^2, has a volume of 100×10^6 m^3 and was formed by the impoundment of the Acaray River.

The Dam was built at 25° 27'36.86"S latitude with SE to NW orientation upstream on the Acaray River, up to the geographic coordinates of 25° 24'31.8"S and 54° 45'54.6"W, where it has its origin [2] just before the river is met by the Yguazú River, where another reservoir, the Yguazú, is located as a compensation lake for the Acaray Reservoir (AR), the two being connected.

Itaipu Binacional has conducted water quality studies in the reservoir [5-10]. Some of these were carried out by Hydroconsult SRL, including the research of the contamination of the bottom sediments by selected 3D elements, Pb and Hg, as well as phosphorus availability by isotopic exchange [11].

As a sink for metals, bottom sediments play a role in the distribution of trace elements. Their dynamics

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also has a function in the fate of these metals throughout the aquatic ecosystem.

The composition of bottom sediments (BS) depends on several factors such as the basin/bed morphology, lithology, weathering/denudation, etc. Geochemistry is primarily controlled by the composition of the source rocks. In the study of sediments, incompatible elements (IE) become very important. IE are those elements that despite the solid fraction are showing the presence of enough octahedral sites to be located into, remain in the magma during its crystallization processes due to their properties of high charge, large radius, etc. Most of them are refractory, that is, they maintain their primary relationships and are transferred almost directly into sediments, being fractioned very little, if at all, by diagenetic and metamorphic processes. Typical IE are rare-earth elements (REE), Zr, Nb, Ba, etc. They are useful tracers of geochemical changes (geoindicators) [12-14].

However, despite their importance, no study has been published with regard to occurrences of rare-earth (REE) and other refractory elements in the Acaray Dam, although they have been investigated in the sediments of the Itaipú Reservoir and other bodies of water in Paraguay [15-18].

The investigation of the presence of IE in the bottom sediments of the AR from its spring down to the dam is the objective of this work. This is a continuation of previous efforts regarding selected elements in the Parana River and tributaries from the right bank (Paraguayan side) as well as in the Itaipú Dam BS [6,9,15,16].

The Sr, Rb, Y, Zr, Nb, Ba, La, Ce, and Nd contents in the bottom sediments of the Acaray Reservoir were investigated by employing the EDXRF analytical technique and their normalised spidergrams were used to look for the *provenance* of the sediments. In addition, the aforementioned values were compared with those found in BS of the Itaipú Lake. The analyses of Fe, Mn and Ti were also performed, since these are usually correlated with the abovementioned elements [19].

The study can be considered a part of the *provenance* studies being carried out in sediments and sedimentary rocks of Eastern Paraguay.

2. EXPERIMENTAL

2.1. Sample preparation

Samples were taken in two different field campaigns with an Eckman dredge from six sampling sites located in the reservoir: ARD: at the upper end of the reservoir; ARB1: after a meander slightly south, at the right bank; ARB2: on the left side, after another meander; D7C: halfway between the B2 stations and the (wall) dam; and D7A1 & D7A2: along the transversal that runs parallel and close to the dam.

In each of these, BS samples were taken in triplicate. Table1 shows their geographic coordinates.

After a preliminary drying under a fan, the samples (composita) were dried in an oven at 120° C for at least 2 hours, then submitted to quartering, and finally ground and sieved. They were prepared in duplicate. For XRF measurements the powdered samples without binders were pressed into pellets of area weight between ~0.1 and 0.3 g cm^{-2}.

Table 1. Sampling stations coordinates

Stations	**latitude**	**longitude**
AR D	25° 25' 06.511" S	54° 42' 39.897" W
AR B1	25° 25' 23.814" S	54° 42' 43.605" W
AR B2	25° 26' 49.390" S	54° 40' 07.045" W
AR C	25° 28' 07.507" S	54° 40' 02.930" W
AR A1	25° 27' 32. 151" S	54° 38' 27.683" W
AR A2	25° 27' 27.945" S	54° 37' 50.614" W

2.2. XRF measurements and analysis

The XRF measurements and quantification were performed utilizing the facilities of the XRF laboratory at the Physics Department, Asunción, Paraguay as well as in the Laboratory of Hydroconsult.

An X-ray tube (at 40kV and 20 mA) with the Mo anode and Mo secondary target as well as the radioisotope source of Am-241 (100 mCi) were used for the excitation of the fluorescence radiation. The energy dispersive X-ray spectrometer attached to the tube excitation system was based on a Si(Li) semiconductor detector (FWHM ≈140 eV at 5.9 keV). The spectrometer with a low-energy GLP Ge planar detector (FWHM ≈210 eV at 5.9 keV) was used with the Am radioisotope source.

The analysis of complex spectra was performed by the AXIL [20] software. The resulting intensities of pure K_α and L_α lines of measured elements were then utilized in the quantitative analysis, employing the quantification software of QAES (Quantitative Analysis of Environmental Samples) designed by P. Kump [21, 22]. This software utilizes the transmission-emission method for determining the absorption in the sample and then iteratively finds the solution of the system of basic XRF equations (one equation for each measured element). The uncertainties of elemental concentrations obtained by the QAES software were assessed to be between 5% and 15% which has been confirmed by the analysis of some standard reference materials (Sediments SL-1 and SL-3 from International Atomic Energy Agency).

3. RESULTS AND DISCUSSION

The mean of absolute values of trace elements Rb-Sr-Y-Zr-Nb-Ba-La-Ce-Nd occurrence in sediments are shown in Table 2. Those of Ti, Mn, and Fe appear in Table 3.

Table 2. Concentration of trace elements (μg g^{-1})

Elements	ARD	ARC	ARB1	ARB2	ARA1	ARA2
Rb	181±17.2	138.2±121.12	135±12.45	128.85±12.67	166.5±16.6	151.5±15.2
Ba	139.8±13.23	281.0±28.81	240.65±21.80	256.5±22.85	256.9±26.6	257±23.2
Nb	14.5±1.9	21.55±2.25	17.0±1.96	19.2±2.58	23.45±2.3	20.7±2.4
La	30.8±2.95	33.20±3.12	25.34±2.35	29.35±2.75	48.55±5.4	44.5±4.6
Ce	46.8±3.9	67.75±5.80	73.8.0±6.53	62.155±5.8	87.9±9.3	126±12.5
Nd	19.4±2.76	18.50±2.35	21.5±2.75	19±2.4	21±3.3	20±2.1
Zr	481±40.99	323.0±33.53	358±36.4	321.5±34	242±22.3	238.4±20.1
Ti	3685±326	7973±669	3338±321.3	7702±817	6176±4.5	5775.5±490
Y	29±2.1	37.32±4.14	36.75±4.74	43.7±4.4	52.8±4.5	38.3±4.5
Sr	18±1.9	27.2±3.4	30.1± 3.2	30.7±3.2	27.95±2.72	26±2.7

Table 3. Concentration of minor elements (mg g^{-1})

Elements	ARD	D7C	D7B1	AR B2	D7A1	AR A2
Ti	3.69±0.33	7.97±0.67	3.34±0.32	7.70±0.82	6.18±0.58	5.78±0.58
Mn	2.44±0.22	2.12±0.18	2.08±0.23	1.92±0.17	1.62±0.18	1.81±0.2
Fe	10.0±1.2	56.30±5.8	64.5±7.2	52.7±5.0	50.50±4.8	57.20±5.4

Just as the Itaipu Dam, the AR is situated in the area of the Alto Paraná Formation (APF) from the lower Cretaceous, which was exposed to extended lava flow represented by tholeiitic basalts [23-26]. On the other hand, the Acaray River flows over sedimentary beds corresponding mostly to sandstones of the Misiones Formation (Jurassic/Cretaceous) and to a much lesser extent over those from the Acaray Formation (Upper Cretaceous) that rest over basalt of the APF (correlated with the volcanic floods of Serra Geral, Brazil) [6] [10]. Although dykes, sills, etc. very often occur in AP Formation, basaltic flows dominate the Cretaceous magmatism in the Paraná Basin. Due to their higher charge and higher crystal energy, rare-earth (REE), and other incompatible elements are unlikely to replace calcium ions from basaltic plagioclase. The sediments derived from mafic igneous rocks should, therefore, have low content of rare-earth elements. However, this is not the case either at AR or in the Itaipú Dam. Their bottom sediments are enriched in LREE and other incompatible elements whose values are higher than those previously mentioned for basaltic rocks and their residual soils or sediments [16,27-29].

Comparing the results found here with those from BS of ID, the values are close to those from the Piratiy and Carapa tributaries (upper stretch) [16], which also flow over sedimentary beds, but lower than the high values found in the samples of sediments from sampling stations on volcanic beds (Pira Pyta, Itabo, Limoy, Itambey). These enhanced values are in agreement with those previously reported by several researchers [30] for the Alto Paraná–Serra Geral basalts.

Metasomatic processes may cause the enrichment of incompatible elements. Such events might be associated with the thermal anomaly, which generated the Paraná Basin flow of tholeiitic basalts [31,32].

These basalts are of two types – one with high TiO_2 (>2 %) and enriched with some IE, and the second with a lower concentration of both TiO_2 and IE, as shown in several studies [28 -30]. As expected, their residual soils are lateritic (Latosol-Oxisol).

The soils derived from the sandstones of the Misiones and Acaray Formations have a large amount of sand particles and are deep and well-infiltrated (Ultisol/sandy Ultisol).

Two refractory elements with an important occurrence in the sediments are Ti and Zr. The measured concentrations of Ti are high and are well-correlated with their tenors in the BS of the ID and with the Ti content of basalts from the Alto Paraná flow. They are in agreement with the fact that in the geochemical cycle, titanium minerals are usually among the unattacked. Zirconium minerals in igneous rocks, especially zircon, are very stable under mechanical stress and chemical weathering. Thus, the major part of the zircon also remains among the unattacked minerals. In the aforementioned basalts, zirconium has been found to be enriched, with respect to niobium. It has been shown that this enrichment in the Earth's mantle could be due to Zr-Nb decoupling under a certain $CO_2/(CO_2+H_2O)$ ratio [31] and is reflected in the sediments (the correlation factor found here for Zr vs Nb, $r = -0.92$).

In regard to them and as other refractory elements analyzed, like REE, Rb, Ba, Y, etc., which stay in the liquid phase during magmatic differentiation, in case they evolved in the same way, they are used to characterize the magma source. To compare their occurrence, the registered values are normalized to a reference standard, which are the values of the Primordial Mantle (PM) [12-14].

The resulting spidergrams in a broad sense present an enrichment of the incompatible elements due to the magma differentiation processes in BS of AR as those found in the Itaipú Dam that are shown in Fig. 1 and 2.

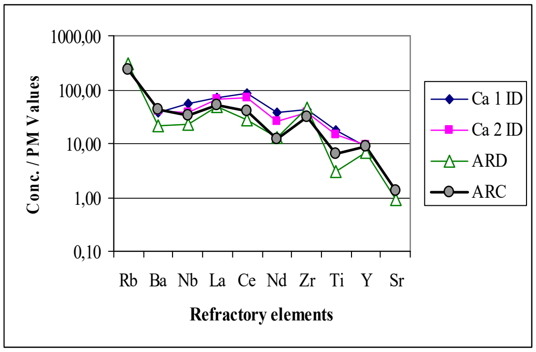

Figure 1. Spidergrams of Acaray Reservoir D and C stations and Ca1 and Ca2 from the Itaipu Dam; PM normalized values

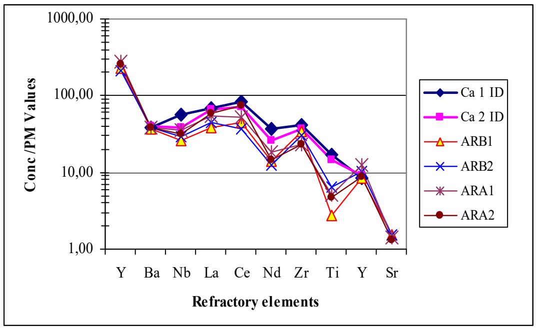

Figure 2. Spidergrams of Acaray Reservoir B1-B2 and A1-A2 stations and Ca1 and Ca2 from the Itaipu Dam; PM normalized values

The negative anomaly of Sr, on the other hand, is indicative of an impoverishment of the melt in this element, which usually accompanies Ca in the plagioclases.

Despite the fact that AR is seated on basalt beds, the multielement-diagrams in the reservoir do not look as those corresponding to an active margin setting. That can be an index of the input of allochthonous materials in both modern and paleo times. Then some modifications in the typical spidergrams of active margin provenance might be expected, as were found here. In addition, iron oxi-hydroxides should, by absorption, become enriched in trace metals in the sediments. The Pearson correlation factors of Fe versus, e.g., La, Ce, Nb, Y are not high (r ~ 0.14, 0.52, 0.55, 0.59 respectively), which is also indicative of some input of exogenous material that could act as a diluent affecting its distribution/concentration in BS.

In order to analyze the components not originating from magma in the BS samples, it is advantageous to normalize the results with the current values assigned to the Upper Crust [33,34]. Thus, when drawing spidergrams (see Fig 3 and 4) of refractory elements in sediments from AR and ID normalized to the Upper Crust values, they are close to 1, suggesting an upper-crust origin. This is indicative of the recycling of materials from the Alto Paraná Formation. The positive spikes of Nb, Ce, and Ti also indicate their enrichment. It should be mentioned that AR sediment spidergrams resemble that of the sandstones of the Misiones Formation traversed by the Acaray River [35]: a trough at Nb and strong negative anomalies at Nd and Ti; a bump at La and a positive spike at Zr.

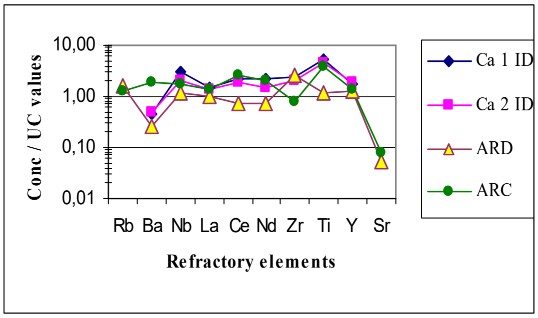

Figure 3. Spidergrams of ARD and ARC stations and Ca1 and Ca2 from the Itaipu Dam; UC normalized values

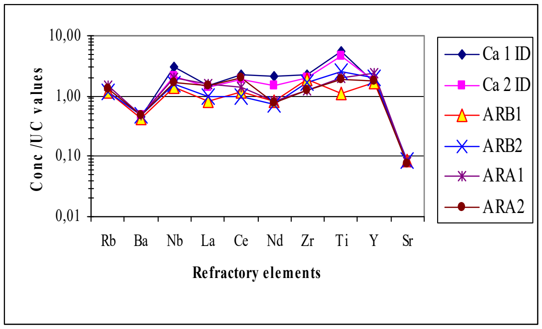

Figure 4. Spidergrams of AR B1-B2 and AR A1-A2 stations and Ca1 and Ca2 from the Itaipu Dam; UC normalized values

This means that AR, seated in an active margin setting, has been subjected to weathering cycles, i.e., in line with studies which indicate that a very large amount of sediments of the Alto Paraná River [16] as well as of other large rivers of the world are recycled sedimentary material [36-40]. In a recent paper employing the very stable isotopic signatures of Sr, Nd, and Pb, it has been shown that about 90–95% of the Amazon River's modern suspended sediments originate in the Andes' recycled materials and, only to a very minor amount, from the Brazilian Shield [41]. Apart from that, the aeolian transport could be significant: ~ 28×10^6 t/yr of Sahara dust are deposited on the Amazon forest, carrying a phosphorus content of~ $0{,}022\times10^6$ t/yr [42].

4. CONCLUSION

As per their PM normalized multielement-diagrams, IE show to be enriched due to magmatic differentiation. In addition, the UC-normalized spidergrams also show/indicate the important contributions of the sedimentary environment, particularly, the Acaray River environment, as was also shown in the Itaipú Dam.

REFERENCES

1. *Balance Hídrico Superficial del Paraguay*, Dirección de Meteorología, Asunción, Paraguay, 1992. (*Surface Water Balance of Paraguay*, Directorate of Meteorology, Asunción, Paraguay, 1992.)
2. *Cartas Nacionales. Hojas SG 21 8;21 7; 21 4;21 3.*, Direccion Instituto Geográfico Militar, Asunción, Paraguay, 1995. (*National Maps. Sheets SG 21 8;21 7; 21 4;21 3.*, Directorate of the Military Geographical Institute, Asunción, Paraguay, 1995.)
3. V. J. Fúlfaro, "Geology of Eastern Paraguay," in *Alkaline magmatism in Central-Eastern Paraguay*, P. Comin-Chiaramonti, C. Gomes, Eds., Sao Paulo, Brasil: Universidad de S. Paulo Editora, 1996, ch. 1, sec. 1.1, pp. 17 – 29.
4. *Acerca de los ríos Acaray y Jejui. Aspectos Hidrológicos*, Informe de Hydroconsult SRL al Ministerio de Obras Públicas, Asunción, Paraguay, 1994. (*About the Acaray and Jejui rivers. Hydrological aspects*, Report of the Hydroconsult SRL to the Ministry of Public Works, Asunción, Paraguay, 1994.)
5. J. L. Scroccaro, "Estudio del Transporte de Sólidos para el Embalse de Itaipu," en *Actas de 1^er^ Seminario de la Itaipú Binacional sobre Medio Ambiente*, Asunción, Paraguay, 1979, pp. 101 – 113. (J. L. Scroccaro, "Study of the Transport of Solids for the Itaipu Reservoir," in *Proc. 1st Binational Itaipu Seminar on the Environment*, Asunción, Paraguay, 1979, pp. 101 – 113.)
6. J. F. Facetti, "Embalse de Itaipu-Aspectos Limnológicos Partes I & II," en *Actas de 2do Seminario da Itaipú Binacional sobre Meio Ambiente*, Foz do Iguazú, Brazil, 1987, pp. 153 – 186. (J. F. Facetti, "Itaipu Reservoir-Limnological Aspects Parts I & II," in *Proc. 2nd Binational Itaipu Seminar on the Environment*, Foz do Iguazú, Brazil, 1987, pp. 153 – 186.)
7. A. V. L. Bittencourt, W. Sanches, "Contribucao ao transporte de sólidos dissolvidos en bacias tributarias do sistema do reservatorio de Itaipu," en *Actas de 2do Seminario da Itaipú Binacional sobre Meio Ambiente*, Foz do Iguazú, Brazil, 1987, pp. 207 – 220. (A. V. L. Bittencourt, W. Sanches, "Contribution to the transport of dissolved solids in tributary streams of the Itaipu reservoir system," in *Proc. 2nd Binational Itaipu Seminar on the Environment*, Foz do Iguazú, Brazil, 1987, pp. 207 – 220.)
8. R. A. Ribeiro Filho, M. Petrere Junior, S. F. Benassi, J. M. A. Pereira, "Itaipú Reservoir limnology: eutrophication degree and the horizontal distribution of its limnological variables," *Braz. J. Biol.* vol. 71, no. 4, pp. 889 – 902, Nov. 2011.
   DOI: 10.1590/S1519-69842011000500010
9. J. F. Facetti-Masulli, M. Bordas, "El Modelo de Lewis y el comportamiento térmico del Lago de Itaipu," *Rev. Soc. Cientif. Paraguay*, vol. 15, no. 2, pp. 137 – 152, 2010. (J. F. Facetti Masulli, M. Bordas, "The Lewis model and the thermal patterns of the Itaipu Lake," *Rev. Soc. Cientif. Paraguay*, vol. 15, no. 2, pp. 137 – 152, 2010.)
10. T. A. Pagioro, S. M. Thomaz, "Longitudinal patterns of sedimentation in deep monomitic subtropical reservoir of Itaipu (Brazil-Paraguay)," *Arch. Für Hydrobiologie*, vol. 154, no. 3, pp. 515 – 528, Jul. 2002.
    DOI: 10.1127/archiv-hydrobiol/154/2002/515
11. F. Flores, J. F. Facetti-Masulli, "Phosphorus availability from bottom sediments of lakes using a nuclear technique," *J. Radioanal. Nucl. Chem.*, vol. 161, no. 1, pp. 239 – 244, Aug. 1992.
    DOI: 10.1007/BF02034897
12. B. P. Roser, R. J. Korsch, "Provenance signatures of sandstone-mud stone suites determined using discriminant function analysis of major element data," *Chem. Geol.*, vol. 67, no. 1-2, pp. 119 – 139, Jan. 1988.
    DOI: 10.1016/0009-2541(88)90010-1
13. D. J. Burnett, D. G. Quirk, "Turbidite provenace in the Lower Palaeozoic Manx Group, Isle of Man: implications for the tectonic setting of Eastern Avalonia," *J. Geol. Soc.*, vol. 158, no. 6, pp. 913 – 924, 2001.
    DOI: 10.1144/0016-764900-205
14. F. Albaréde, *Geochemistry: An Introduction*, Cambridge, UK: Cambridge University Press, 2003, ch. 8 sec. 8.3-8.4 pp. 155 – 163, app. A, pp. 207 – 209.
    DOI: 10.1180/0671322
15. J. F. Facetti-Masulli, P. Kump, Z. Villanueva de Diaz, "Selected trace and minor elements in sediments of Itaipu Dam Reservoir," *Czechoslovak J. Phys.*, vol. 53, suppl. 1, pp. A209 – A215, Jan. 2003.
    DOI: 10.1007/s10582-003-0027-6
16. J. F. Facetti-Masulli, P. Kump, Z. Villanueva de Diaz, V. R. de González, "Incompatible elements in bottom sediments of the Itaipu Dam Reservoir by EDXRF," *J. Radioanal. Nucl. Chem.*, vol. 316, no. 2, pp. 861 – 868, May 2018.
    DOI: 10.1007/s10967-018-5801-9
17. J. F. Facetti-Masulli, P. Kump, "Selected minor and trace elements from water bodies of Western Paraguay," *J. Radioanal. Nucl. Chem.*, vol. 286, no. 2, pp. 441 – 448, Nov. 2010.
    DOI: 10.1007/s10967-010-0775-2
18. J. F. Facetti-Masulli, F. Flores, P. Kump, "Geochemical studies and elemental contaminants in the Bay of the City of Asunción," *J. Chem. Chem. Eng.*, vol. 7, no. 11, pp. 1060 – 1067, 2013.
    DOI: 10.17265/1934-7375/2013.11.009
19. K. Rankama, T. Sahama, *Geoquímica*, Madrid, España: Aguilar, 1954. (K. Rankama, T. Sahama, *Geochemistry*, Madrid, Spain: Aguilar, 1954.)
20. P. Van Espen, H. Nullens, F. Adams, "A computer analysis of X-Ray Fluorescence spectra," *Nucl. Instrum. Methods,* vol. 142, no. 1-2, pp. 243 – 250, Apr. 1977.
    DOI: 10.1016/0029-554X(77)90834-5
21. P. Kump, *QAES Instruction Manual*, J. Stefan Institute, Ljubljana, Yugoslavia, 1988.
22. P. Kump, M. Necemer, P. Kupnic, "Development of the Quantification procedures for *in situ* XRF analysis," in *In situ applications of X Ray Fluorescence Techniques, IAEA-TECDOC-1456,* Vienna, Austria: IAEA, pp. 217 – 229.
    Retrieved from: https://www-pub.iaea.org/MTCD/Publications/PDF/te_1456_web.pdf;
    Retrieved on: Jun. 18, 2018
23. A. Melfi, E. Piccirillo, A. Nardy, "Geological and magmatic aspects of the Paraná basin- An Introsuccion," in *The Mesozoic flood volcanism of the Parana Basin petrogenetic and geophysical aspects,* E. M. Piccirillo, A. J. Melfi, Eds., Sao Paulo, Brazil: Instituto Astronómico e Geofísico University of San Paulo, 1988, ch. 1, sec. I.1, pp. 1 – 14.
24. P. Comin-Chiaramonti, P. Cundari, J. M. De Graaf, C. B. Gomez, E. M. Piccirillo, "Early Cretaceous magmatism in Eastern Paraguay (Western Paraná basin); geological, geophysical and geothermal relationships," *J. Geodyn.*, vol. 28, no. 4-5, pp. 375 – 395, Nov-Dec. 1999.
    DOI: 10.1016/S0264-3707(99)00016-2
25. M. Ernesto et al., "Paraná Magmatic Province-Tristan da Cunha Plume System fixed vs mobile plume, petrogemetic considerations and alternative heat source," *J. Volcanol. Geotherm. Res.*, vol. 118, no. 1-2, pp. 527 – 553, Nov. 2002.
    DOI: 10.1016/S0377-0273(02)00248-2
26. P. Comin-Chiaramonti, C. B. Gomes, A. Cundari, F. Castorina, P. Censi, "A review of carbonatitic magmatism in the Parana-Angola-Namibia (PAN)

System," *Periodico di Mineralogica*, vol. 76, no. 2-3, pp. 25 – 78, 2007.
Retrieved from: http://www.dst.uniroma1.it/riviste/permin/testi/V76.DI/2007PM0016.pdf;
Retrieved on: Jun. 23, 2018

27. G. Belliene, P. Comin-Chiaramonti, L. S. Masques, A. J. Melfi, A. J. Nardy, "Petrogenetic aspects of acid and basaltic lavas from the Parana plateau Brazil: Geological, Mineralogical and Petrochemical relationships," *J. Petrol.*, vol. 27, no. 4, pp. 915 – 944, Aug. 1986.
DOI: 10.1093/petrology/27.4.915
28. E. M. Piccirillo, M. Civetta, "Regional variations within the Parana flood basalts (Southerns Brasil) for subconatinetnal mantle heterogeneity," *Chem. Geol.*, vol. 75, no. 1-2, pp. 103 – 122, Feb. 1989.
DOI: 10.1016/0009-2541(89)90023-5
29. G. Bellieni et al., "Continental flood basalts from the central –western regions of the Paraná plateau (Paraguay and Argentina): petrology and petrogenetic aspects," *Neues Jahr. Miner. Abh.*, vol. 154, pp. 111 – 139, 1986.
30. E. M. Piccirillo et al., "Bimodal fissural volcanic suites from the Parana basin (Brazil): K-Ar ages, Sr isotopes and geochemistry," *Rev. Geochem. Bras.*, vol. 1, pp. 53 – 69, 1987.
31. M. Menzies, N. Rogers, A. Tindle, C. Hawkesworth, "Metasomatic and Enrichment Pocesses in Lithospheric Peridotites, an Effect of Athenosphere-lithosphere Interaction," in *Mantle Metasomatism*, M. A. Menzies, C. J. Hawkesworth, Eds., London, UK: Academic Press, 1987, ch. 8, sec. III, pp. 316 – 334.
32. P. Comin-Chiaramonti, G. Demarchi, V. A. V. Girardi, F. Princivalle, S. Sinigoi, "Evidence of mantle metasomatism and hetereogeneity from peridotite inclusions of northeastern Brazil and Paraguay," *Earth Planet. Sci Lett.*, vol. 77, no. 2, pp. 203 – 217, Mar. 1986.
DOI: 10.1016/0012-821X(86)90161-5
33. S. R. Taylor, S. M. McLennan, "The geochemical evolution of the continental crust," *Rev. Geophys.*, vol. 33, no. 2, pp. 241 – 265, May 1995.
DOI: 10.1029/95RG00262
34. S. M. McLennan, "Relationship between trace element composition of sedimentary rocks and upper continental crust," *Geochem. Geophys. Geosyst.*, vol. 2, no. 4, pp. 17, Apr. 2001.
DOI: 10.1029/2000GC000109
35. J. F. Facetti-Masulli, P. Kump, E. Gonzalez-Erico, "Selected trace and minor elements in sandstones from Paraguay," *Radiochim. Acta*, vol. 98, no. 7, pp. 441 – 446, 2010.
DOI: 10.1524/ract.2010.1734
36. M. Dellinger et al, "Li isotope fractionation in the Amazon River basin controlled by the weathering regimes," *Geochim. Cosmochim. Acta*, vol. 164, pp. 71 – 93, Sep. 2015.
DOI: 10.1016/j.gca.2015.04.042
37. J. Gaillardet, B. Dupre, C. J. Allegre, "Geochemistry of large river suspended sediments: what can we learn about present day weathering of silicates?" *Mineralogical Magazine*, vol. 62, pp. 489 – 490, 1998.
DOI: 10.1180/minmag.1998.62A.1.259
38. J. Gaillardet, B. Dupre, P. Louvat, C. J. Allegre, "Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers," *Chem. Geol.*, vol. 159, no. 1-4, pp. 3 – 30, Jul. 1999.
DOI: 10.1016/S0009-2541(99)00031-5
39. S. Yang, H. S. Jung, C. Li, "Two unique weathering regimes in the Changjiang and Huanghe drainage basins: geochemical evidence from river sediments," *Sedimentary Geology*, vol. 164, no. 1-2, pp. 19 – 34, Feb. 2004.
DOI: 10.1016/j.sedgeo.2003.08.001
40. L. Bastian, M. Revel, G. Bayon, A. Dufour, N. Vigie, "Abrupt response of chemical weathering to Late Quaternary hydro-climate changes in Northeast Africa," *Sci. Rep.*, vol. 7, 44231, 2017.
DOI: 10.1038/srep44231
41. N. Höppner, F. Lucassen, C. M. Chiessi, A. O. Sawakuchi, S. Kasemann, "Holocene provenance shift of suspended particulate matter in the Amazon River basin," *Quaternary Sci. Rev.*, vol. 190, pp. 66 – 80, Jun. 2018.
DOI: 10.1016/j.quascirev.2018.04.021
42. H. Yu et al., "The fertilizing role of African dust in the Amazon rainforest: A first multiyear assessment based on data from Cloud‐Aerosol Lidar and Infrared Pathfinder Satellite Observations," *Geophys. Res. Lett.*, vol. 42, no. 6, Mar. 2015.
DOI: 10.1002/2015GL063040