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Selected minor and trace elements from water bodies of western Paraguay

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Abstract Minor and trace elements composition of bottom sediments from water bodies in Western Paraguay have been investigated by XRF techniques to determine their correlation as well as provenance. The analysis of complex spectra was performed by the AXIL software and the quantitative analysis by the QAES software. Analyzed trace elements were the refractory elements Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pr, Nd, Zr, y and other HFSE as Cr, Ni, Cu, together with Zn. Minor elements were Ti, Mn, Fe which are often to the above refractories related. According to their normalized spidergrams two sets of sediments can be differentiated. Those from Pilcomayo and Verde rivers as well as from km164-Wetland show light rare earth elements (LREE) enrichment, negative Nb and Ti anomalies and no spike at Zr. On the other hand, sediments from Confuso, Aguaray(Jehe), Negro and Montelindo rivers have spidergrams very alike, with strong negative anomalies at Nb, Nd and Ti whereas a positive at Zr. Further, in the former there is a strong correlation of Fe versus the refractory elements; such a correlation does not exist in the latter. The sediments from the Pilcomayo & Verde Rivers and from the km164-Wetland evolved as the sub-Andean/Andean metamorphic/sedimentary materials.

Keywords Bottom sediments · Western Paraguay · Chaco rivers · XRF · Refractory elements · LREE · Andean · Denudation · Recycled

Introduction

The western region of Paraguay or Chaco Boreal is seated between two rivers, the Paraguay River to the East and the Pilcomayo River to the South. It covers an alluvial plain of 247,150 km^2, consisting of unconsolidated sediments from the Tertiary and Quaternary ages [1].

The Paraguay River is the main tributary of the Parana River. The stretch from the mouth of the Apa River to its outlet on the Parana River has an extension of ~890 km and a discharge of ~2,000 m^3/s; upstream the discharge is ~1,500 m^3/s. Together these rivers, Paraguay-Parana, constitute a system which is within the first 15 of the largest rivers in the world. Along its right side, the flood plain of the Paraguay River is a low lying area of about 60–100 km wide. The Pilcomayo River, on the other hand, starts in the Andes Mountains above 3,900 m of altitude and, as a constituent of the border between Paraguay and Argentina, the Pilcomayo is an international river. Along the left of the Pilcomayo its flood area covers ~17,500 km^2 [2].

This river carries a large amount of sediments (9.8×10^7 ty^{-1}); at the *Upper Pilcomayo* during the flood periods the current has very strong effects on the meanders, with erosion on the concavities and embankment on the convexities; this changes the axis of the draining channel of the Pilcomayo.

When loosing velocity (*Middle Pilcomayo*) the sediments settle down generating bars that interrupt the stream and the river starts rambling: the water overflows,

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originating marshes, ponds, etc., that during the flood periods can form extended areas of open water. Another effect of this prominent deposition is the progressive regression of the river upstream. Thus, the river vanishes but appears again downstream (*Lower Pilcomayo*) with much lower flow. This occurs about 250 km from its mouth on the Paraguay River. In regard to this river, the contribution of sediments from the Pilcomayo nowadays is not very much important; a prominent part of its total suspended solids (TSS) is due to the discharge of the Bermejo River, more to the south of the Pilcomayo.

In addition, and sustained by this yearly overflow, the Pilcomayo River nourishes a large quantity of aquifers as well as other rivers that run on the so called alluvial fan-shaped plain of the Pilcomayo, for example the Confuso, Acaray, Negro, Montelindo, etc.; thus, the flood periods of these are related to the flood periods of the former. However, a relationship in their origin is unknown. Therefore, a study of the *provenance* of the sediments would be appropriate in order to elucidate the point.

The composition of the sediments depends on several factors and the geochemistry is primarily controlled by the composition of the source rocks.

Western Paraguay, is a low and extended alluvial plain. The so called Chaco Formation is a sedimentary and structural basin with very little orographic expression. This region was the northern part of a "geosyncline" existing in the south central part of South America; it was covered by a proto-Pacific sea [1].

This geosyncline is limited in the north by the mountain chain of San Jose and Santiago in Bolivia, with rocks of the lower Paleozoic. In the west is limited by the sub-Andean mountains also in Bolivia, formed by rocks from of the Paleozoic, Triassic, upper Cretaceous and Tertiary [3]. In the eastern part, the limit is defined by the Asunción Arc, constituted by limestones of the lower Paleozoic, sandstones of the Gondwana and from Fuerte Olimpo to Asunción, in three different outcrops, by rhyoliths, alkalic rocks and nephenilites/fonolites, from the Proterozoic [4, 5], Permo-Triassic [6] and from the Tertiary [7] all of them on the right side of the Paraguay River.

The basin shifted over the continental crust as a result of the Brasiliano events in the Cambrian (680–450 Ma). The orogenic cycle of the Paleozoic developed the formation of an orogen during the upper Silurian/lower Devonian that presents a remarkable differentiation from a continental passive margin in a wide proto-Pacific bay to an active margin, the sediments resting in unconformity. In the Mesozoic two main events can be distinguished: the Sub-Atlantic Cycle (Triassic/lower Jurassic) and the Andean Cycle (Upper Cretaceous/Tertiary) highly affected by the uprising of the Andean mountains and the processes of sedimentary filling of the Mesozoic basins.

Rocks of Silurian and Devonian age with a high grade of metamorphism constitute the basement of such an extended depression, which is filled in by sediments of several origins that settled in a shallow marine surrounding. In the Devonian/upper Permian, the sediments were sandy as well as in the Mesozoic. In the Tertiary, sedimentation ($\sim$1,600 m in thickness) occurred in the Neogene; more to the surface they are from the Quaternary (Pliocene and Pleistocene). At depths between 100 and 200 m the environment is marine; above it is continental [8].

In this work using XRF analytical techniques the Rb, Sr, Y, Zr, Nb, Ba, La, Pr, Ce, and Nd contents in bottom sediments of the main tributaries on the right side of the Paraguay River were investigated focusing on their geochemistry; their normalised spidergrams were used to elucidate their *provenance;* additionally the aforementioned values were compared with those found in rocks from the sub-Andean and Andean areas. The analyses of some elements from the "*3d*" series were also performed.

This work can be considered as an extension of the other *provenance* studies being carried out on sediments and sedimentary rocks of Paraguay.

Experimental

Samples

Samples were taken in three different field campaigns with an Eckman dredge from six sampling stations located at sections of five tributaries of the Paraguay River and at a Wetland. These sections from north to south are: Verde (V) S23° 12,932′ W59° 12,096′, Montelindo (ML) S23°15,590′ W58° 18,00′ and Negro (N) S24° W58° 16,537′ Rivers; km164-Wetland (W) S24° 15,541′ W58° 16,537′; Aguaray (AG) S24° 34,773′ W58° 02,142′ and Confuso (CO) S24° 54,681′ W57° 40,550′ Rivers. Sediments of the Pilcomayo River were also investigated upstream in two sites (Pozo Hondo & Pedro Peña labeled P1 and P2) of the stretch where the river flows permanently, before (P1, P2) and after the flood period (P3). In each of these, sediments samples were taken in triplicate. Composite samples were prepared by quartering after being dried in an oven at 120 °C, ground and sieved.

XRF measurements and analysis

Procedures

The procedures were carried out in Asunción, at the Hydroconsult Laboratory and in Ljubljana, at the XRF-Laboratory of J. Stefan Institute. For XRF measurements the finely pulverized materials (particle size ≤ 30 μm) were pressed into pellets of area mass of ~ 0.1–0.3 g cm^{-2} and were transparent at the energy of the Mo K_α, which was used as a target in the transmission–emission procedure employed in the quantification process.

The excitation of fluorescence radiation by the radioisotope sources of Cd-109 (20 mCi), Fe-55 (20 mCi) and Am-241 (50 mCi) was utilized. The energy dispersive X-ray spectrometer was based on a Si(Li) semiconductor detector (FWHM $\approx$ 140 eV at 5.9 keV). The spectrometer with low energy GLP Ge planar detector (FWHM $\approx$ 210 eV at 5.9 keV) was used with the Am radioisotope source. The analysis of complex spectra was performed by the AXIL [9] software which is based on iterative nonlinear least square fit of the spectra by the gaussian shaped spectral lines. The resulting intensities of pure K_α and L_α lines of measured elements were then utilized in quantitative analysis, employing the quantification software of QAES (quantitative analysis of environmental samples) designed by P. Kump [10]. This software utilizes the i.e. transmission–emission method for determination of the absorption in the sample and then iteratively finds the solution of the system of basic XRF equations (for each measured element there is one equation). The basic XRF equation namely relates the measured intensity to the respective concentration of the element in the sample. Since this relation is nonlinear and the intensities depend also on concentration of unmeasured elements, the information on the absorption in the total sample is crucial in solving such a system of equations. On the other hand the quantification would be possible only if a set of standards very much resembling the unknown samples would be at hand to perform the necessary calibrations. The absorption measurement on the sample was in principle equivalent to additional measurements on a set of standards.

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 certified reference materials (RM Soil-7, Sediments SL-1 and SL-3 from International Atomic Energy Agency, and Montana soil SRM 2710 from NIST).

Results and discussion

The average of the absolute values of "*3d*" elements occurrence are shown in the Table 1; those of Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Nd in the Table 2.

Generally, the "*3d*" elements do not maintain the original geochemical composition of the precursor materials. The elements are considered mobile and this mobility is related to their oxidation states: is very low for states +3 and +4 and fairly high for the +2 state. As they usually do not precipitate directly (but Fe and Mn), their incorporation into sediments are mainly due to co-precipitation processes; elements like Ti, Mn and Fe are related to the refractories. Their spidergrams (Fig. 1) present the typical "in *W* distribution" of Allegre [11]. During the crystallization processes of the magma, the solid fraction shows enough octahedral sites; elements such as Cr^{+3} and Ni^{+2} become stabilized in that octahedral environment while Mn^{+2} and Zn^{+2}, which have the *"d"* orbitals half-filled and filled respectively, are not as much effected by the crystal field. As an example, for Cr^{+3}, "d^3" ion the crystal field stabilization energy (CFSE) is $-6/5\Delta q$, whereas Mn^{+2}, "d^5" low field ion, have CFSE $= -3{*}2/5\Delta + 2{*}3/5\Delta = 0$.

Those elements with high stabilization energy are located in such sites and their partition coefficients (exponential function of the bonding energy) are high as well. Thus, they stay more stabilized in the solid but in the magma they become depleted. One can see this in the normalized multi-element diagrams of Fig. 1, with chromium and nickel at the bottoms of the troughs, whereas manganese and zinc are at the higher peaks.

In regard to the refractory elements studied, their occurrence in the sediments are lower than those from the Itaipú Dam [12], (Alto Parana Formation, mainly tholeiitic basalts) but nearly the same as those presented by materials from the subAndean/Andean regions [3, 13, 14]. These elements are often used as *provenance* indicators. They are refractory as well as their compounds. Usually they maintain their primary relationships and are transferred almost directly into sediments, being fractioned very little, if at all, by diagenetic and metamorphic processes.

Trace metals can be absorbed by iron oxy-hydroxides in sediments. Therefore, the correlation factors were calculated with a 95% of confidence. The results for the km164-Wetland, Verde and Pilcomayo Rivers are as follows: La–Fe: $r = 0.94$; Ce–Fe: $r = 0.97$; Nd–Fe: $r = 0.97$; Zr–Fe: $r = 0.1$; Nb–Fe: $r = 0.93$, Ti–Fe: $r = 0.63$, and Ba–Fe: $r = 0.93$. On the other hand such strong correlations of these elements in the Confuso, Aguaray, Negro and Montelindo Rivers do not exist.

Also Ti shows good correlations with the incompatible elements in the samples of the firstly mentioned set of rivers: La–Ti: $r = 0.64$; Ce–Ti: $r = 0.66$; Nd–Ti: $r = 0.58$; Nb–Ti: $r = 0.66$, Ti–Zr: $r = 0.34$, Ti–Ba: $r = 0.56$. The second set of rivers does not present such correlations. From this point of view, two sets of water bodies can be differentiated. One set includes the Confuso, Aguaray, Negro and Montelindo Rivers and the other, the Pilcomayo itself, the km-164 Wetland, and the Verde River.

Table 1 Concentration of “*3d*” elements

	W1	W5	W7	ML1	ML5	ML7	V1	V5	V7
mg.g^{-1}									
Ti	4.28 ± 0.27	4.32 ± 0.32	4.77 ± 0.3	3.24 ± 0.21	1.89 ± 0.15	3.82 ± 0.25	2.78 ± 0.19	2.35 ± 0.12	1.86 ± 0.14
Mn	0.541 ± 0.04	0.52 ± 0.05	0.53 ± 0.04	0.16 ± 0.02	0.93 ± 0.07	0.66 ± 0.05	0.54 ± 0.04	0.53 ± 0.03	0.48 ± 0.04
Fe	27.1 ± 1.6	30.9 ± 2.1	23.4 ± 1.3	9.6 ± 0.6	11.9 ± 0.8	22.7 ± 1.3	18.5 ± 1.0	19.6 ± 1.1	21.7 ± 1.25
μg g^{-1}									
Cr	300 ± 29	280 ± 20	263 ± 28	253 ± 27	228 ± 23	261 ± 27	215 ± 25	208 ± 24	192 ± 23
Cu	9.4 ± 7.2	NA	94.1 ± 7.1	83 ± 6	NA	89.7 ± 6.8	79.0 ± 6.2	81.0 ± 6.3	83.1 ± 6.5
Ni	23.4 ± 4.0	62.5 ± LOD	27.7 ± 4.4	10.5 ± LOD	63.4 ± LOD	13.4 ± 3.6	17.1 ± 3.4	13.2 ± LOD	12.6 ± 3.4
Zn	81.6 ± 6.0	41.2 ± 12.8	86.0 ± 6.2	36.7 ± 3.4	57.8 ± 12.6	75.3 ± 5.6	52.9 ± 4.0	60.8 ± 6.2	66.4 ± 5.1

	P1	P2	P3	CO1	CO5	CO7	AG1	AG7	N1	N5	N7
mg g^{-1}											
Ti	5.11 ± 0.36	4.34 ± 0.32	4.22 ± 0.34	1.57 ± 0.13	3.07 ± 0.23	2.10 ± 0.16	2.25 ± 0.16	2.91 ± 0.19	4.06 ± 0.26	1.87 ± 0.14	2.69 ± 0.18
Mn	1.10 ± 0.08	1.02 ± 0.08	1.10 ± 0.08	0.71 ± 0.06	1.33 ± 0.10	0.41 ± LOD	0.12 ± 0.02	0.16 ± 0.02	0.24 ± 0.02	0.38 ± 0.03	0.15 ± 0.02
Fe	41.6 ± 2. 9	41.4 ± 2.5	42.06 ± 2.18	8.97 ± 0.62	20.1 ± 1.4	8.9 ± 0.6	6.23 ± 0.36	9.27 ± 0.54	13.5 ± 0.8	8.15 ± 0.56	11.3 ± 0.7
μg g^{-1}											
Cr	126 ± 32	142 ± 50	138 ± 44	103 ± 28	134 ± 31	127 ± 23	221 ± 25	210 ± 24	254 ± 3	196 ± 19	169 ± 23
Cu	NA	NA					68.5 ± 5.5	78.7 ± 6.1	83.0 ± 6.4	NA	70.1 ± 5.8
Ni	67.8 ± LOD	57.6 ± 10	61.6 ± 7.0	70.4 ± LOD	48.2 ± LOD	41.1 ± LOD	7.31 ± LOD	6.7 ± LOD	13.6 ± LOD	69.8 ± LOD	8.35 ± LOD
Zn	110 ± 13	106 ± 14.7	112 ± 11	85.6 ± 13.8	82.7 ± 13.6	108 ± 12	24.7 ± 2.7	43.6 ± 3.7	46.7 ± 3.9	86.5 ± 10.7	35.9 ± 3.3

NA not analyzed

Table 2 Concentration of refractory elements

	W1	W5	W7	ML1	ML5	ML7	V1	V5	V7
μg g^{-1}									
Rb	112 ± 7	158 ± 18	113 ± 7	59.8 ± 3.6	110 ± 14	92.4 ± 5.6	74.8 ± 4.5	87.8 ± 4.2	90.5 ± 5.6
Sr	123 ± 7	111 ± 15	134 ± 8	86.6 ± 5.2	195 ± 11	126 ± 7	121 ± 13	120 ± 9	130 ± 8
Y	23.6 ± 1.7	13.7 ± 3.7	20.1 ± 1.5	14.2 ± 1.2	7.95 ± LOD	20.5 ± 1.5	15.7 ± 1.3	16.9 ± 0.9	18.9 ± 1.4
Zr	254 ± 15	258 ± 19	193 ± 13	501 ± 31	211 ± 15	222 ± 15	204 ± 13	192 ± 13	189 ± 13
Nb	9.6 ± 0.7	24.7 ± 5.8	12.2 ± 2.6	5.96 ± LOD	8.7 ± 3.6	11.3 ± 2.5	6.51 ± LOD	6.9 ± 1.3	7.2 ± 2.4
Ba	703 ± 42	533 ± 4	405 ± 25	317 ± 20	420 ± 29	402 ± 25	395 ± 24	396 ± 18	402 ± 25
La	24.2 ± 1.5	49.7 ± 5.7	26.8 ± 3.1	13.5 ± 2.2	20 ± 3	25.2 ± 2.9	15.1 ± 2.2	16.5 ± 1.7	17.9 ± 2.6
Ce	64.1 ± 3.8	91.4 ± 8.2	56.2 ± 4.6	36.1 ± 3.4	54.4 ± 4.3	54.4 ± 4.3	37.7 ± 3.3	45.8 ± 4.2	45.5 ± 4
Pr	8.10 ± 1.23	11.0 ± LOD	8.8 ± 2.6	7.1 ± 1.0	6.85 ± LOD	7.23 ± 1.0	5.1 ± 1.0	5.5 ± 1.1	6.1 ± 0.9
Nd	29.0 ± 1.6	33.0 ± 6.6	29.6 ± 4.3	15.3 ± 3.4	22 ± 4	24.5 ± 3.8	21.5 ± 3.4	23.2 ± 2.0	20.7 ± 3.8

	P1	P2	P3	CO1	CO5	CO7	AG1	AG7	N1	N5	N7
μg g^{-1}											
Rb	209 ± 18	222 ± 21	216 ± 13	73.5 ± 12.6	132 ± 16	105 ± 12	39.8 ± 3.0	61.3 ± 3.8	72.9 ± 4.4	107 ± 11	65.1 ± 3.9
Sr	172 ± 15	146 ± 17	146 ± 13	95.1 ± 12.9	109 ± 14	94.3 ± 11	63.4 ± 3.8	85.8 ± 5.1	91.5 ± 5.4	88.8 ± 10.2	90.9 ± 5.4
Y	19.5 ± 3.7	16.9 ± 4.0	17 ± 2.7	7.64 ± LOD	10.9 ± 3.1	8.64 ± 0.8	9.7 ± 0.9	13.8 ± 1.2	18.1 ± 1.4	8.24 ± 2.75	14.7 ± 1.2
Zr	271 ± 20	142 ± 12	189 ± 11	317 ± 24	444 ± 31	339 ± 23	286 ± 34	286 ± 17	341 ± 21	353 ± 25	289 ± 18.5
Nb	31.1 ± 5.3	28.9 ± 5.9	30 ± 4.0	9.64 ± 4.07	22.7 ± 5.0	10.8 ± 1.2	4.57 ± LOD	6.31 ± 0.51	8.43 ± 2.3	8.29 ± LOD	15.3 ± 2.7
Ba	839 ± 57	961 ± 66	910 ± 44	404 ± 28	1,720 ± 115	377 ± 25	273 ± 17	288 ± 17	365 ± 22	399 ± 28	353 ± 22
La	51.5 ± 5.4	59.7 ± 6.4	56 ± 4	20.7 ± 3.3	24.2 ± 5.1	20.5 ± 1.5	14.1 ± 2.0	14.7 ± 0.9	21.8 ± 2.5	18.9 ± 3.1	18.7 ± 2.6
Ce	102 ± 8.3	111 ± 10	107 ± 6	45.6 ± 4.5	76.3 ± 6.8	45.4 ± 3.1	29 ± 2.9	32.9 ± 2.0	44.6 ± 3.7	47 ± 4.8	47.3 ± 4.1
Pr	10.3 ± 4.0	15.4 ± 6.0	13.3 ± 3.5	7.9 ± LOD	10.6 ± 4.5	2.2 ± 0.8	6.6 ± 1.8	5.9 ± LOD	–	10.9 ± LOD	8.66 ± 2.0
Nd	48.3 ± 6.3	57.2 ± 7.7	53 ± 4.2	17.8 ± 4.1	38.0 ± 6.7	16.1 ± 1.5	9.49 ± LOD	12 ± 0.9	17.5 ± 3.4	13.0 ± 4.4	21.2 ± 3.9

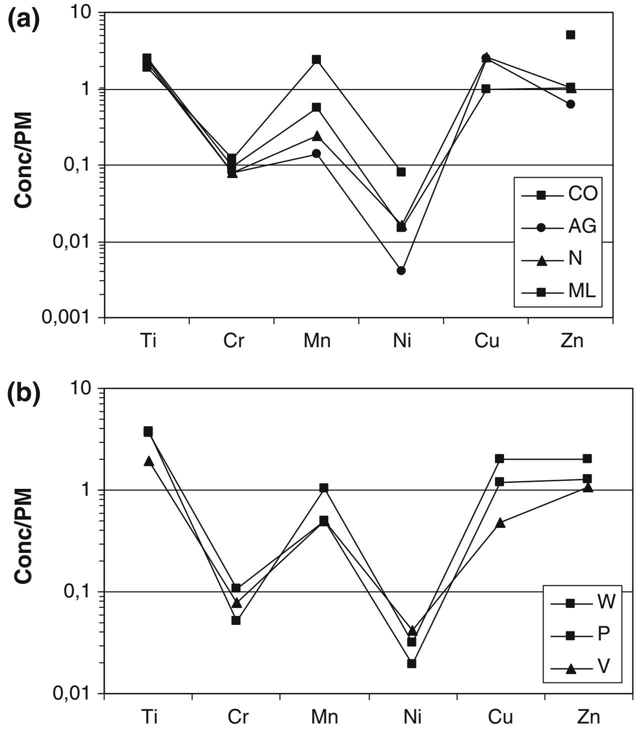

Fig. 1 **a** Normalized to Primordial Mantle "*3d*" element spidergrams of Confuso, Aguaray, Negro and Montelindo Rivers. **b** Normalized to Primordial Mantle "*3d*" element spidergrams of km164-Wetland and Pilcomayo and Verde Rivers

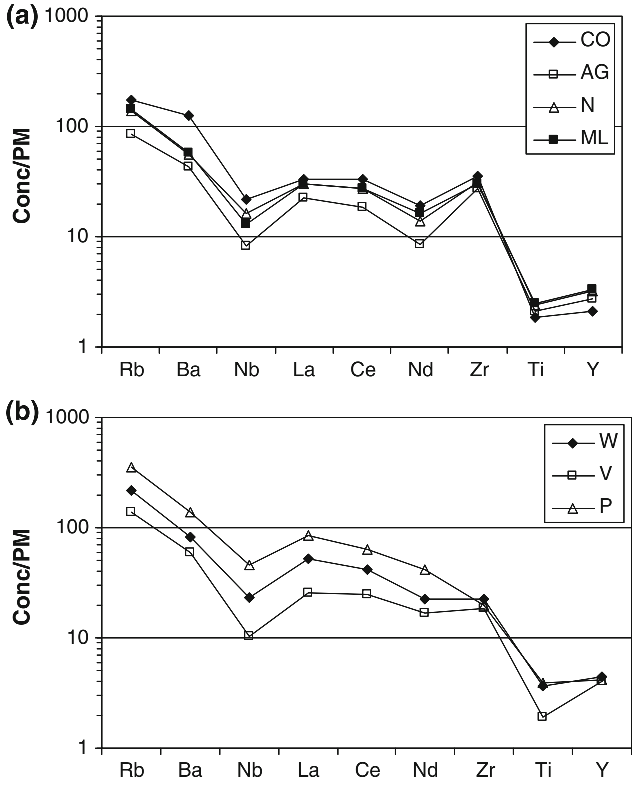

Fig. 2 **a** Normalized to Primordial Mantle refractory element spidergrams of Confuso, Aguaray, Negro and Montelindo Rivers. **b** Normalized to Primordial Mantle refractory element spidergrams of km164-Wetland, Verde and Pilcomayo Rivers

Magmas intruding into the crust are previously subjected to differentiation. Some elements due to their properties stay in the liquid phase and are labeled incompatible; provided they evolved in the same way, such as REE and other refractories, they are used to characterize the magma source [15] and are geochemical indicators. To compare their occurrence, the analyzed values must be normalized to a reference standard, which in this work are the values of the Primordial Mantle (PM)[16].

REE are lithophilic; with regard to their similar ionic radii they fit into crystal lattice of Ca^{+2} bearing minerals. But when such minerals are in equilibrium with silicate melts, due to their higher charge and higher crystal energy, those elements become concentrated in the melt. Thus, when a portion of mantle, known to be similar in composition to the chondrites [17, 18], forms a basaltic melt, such elements become enriched in the liquid phase, and the solid peridotite stays depleted in REE.

According to the spidergrams of analyzed refractory elements (Sr is not included), the Confuso, Aguaray, Negro and Montelindo Rivers present (see Fig. 2a) an enrichment of the incompatible elements due to the magma differentiation processes. They also show deep troughs at Nb and Ti, a positive anomaly at Zr and a close resemblance to the spidergrams of sandstones from the Carboniferous/Permian ages [19] of Eastern Paraguay and to a passive continental margin setting [20, 21].

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 and which is also present *diadocia* with K.[22], with prominent expression, 1.3–2.6% (not shown in Tables 1, 2) in the samples. On the other hand, Ba does not replace Ca in the plagioclases but presents *diadocia* with Rb. The values found are compatible with those given by Rankama [22] and point toward felsic source rocks.

Samples from the water bodies of the other set, i.e., the km164-Wetland, the Verde and Pilcomayo Rivers, present spidergrams that show equally well the enrichment of the incompatibles including Ti (see Fig. 2b). They are very similar to each other, but different from the former set: a small trough at Nb, a bump at La, no spike at Zr, and higher values at the Ti troughs, that can be indicative of an active continental margin setting. In addition it is worthwhile to mention that these spidergrams are very much alike, with remarkable similarities to those published recently in regard to studies made on rocks from the sub-Andean/Andean regions of Bolivia [5] and in the Andean northwest region of Argentina [14 & Ref there in] close to the border

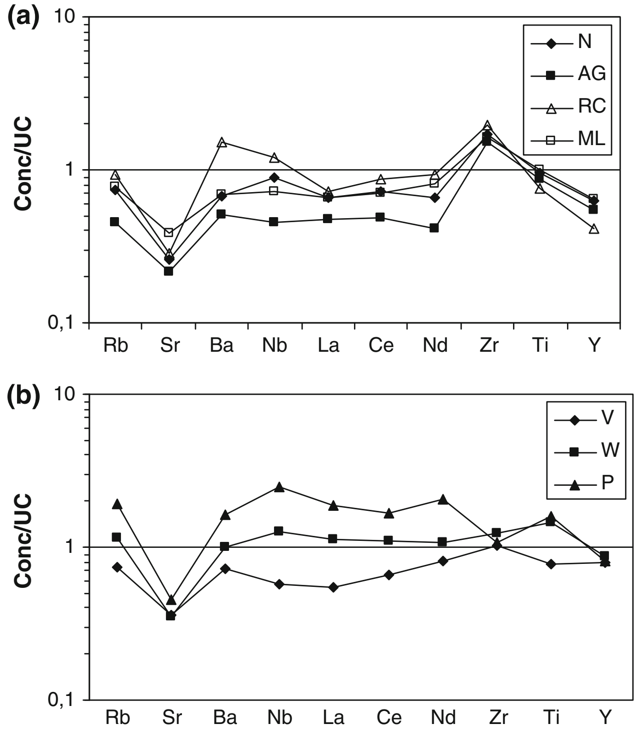

Fig. 3 **a** Normalized to Upper Crust refractory element spidergrams of Confuso, Aguaray, Negro and Montelindo Rivers. **b** Normalized to Upper Crust refractory element spidergrams of km164-Wetland, Verde and Pilcomayo River

with Paraguay. Therefore, they should have had the same *provenance,* and have been submitted to similar processes from Paleozoic to Recent times. In such a case one can conclude that the sediments are products of the recycling of the magmatic, metamorphic and sedimentary materials produced and processed during and after the Paleozoic Era, the Sub-Atlantic and the Andean Cycles, the uprising of the Andean mountains etc.

For comparison, according to published results, [23], it is also interesting to mention that the spidergram of the total suspended solids (TSS) from the Pilcomayo River is very similar to those from its bottom sediments (See Table 2; Fig. 2b) and that the Parana-Paraguay River system present also at their TSS similar signature from an Active Continental Margin setting.

In addition, when drawing spidergrams (see Fig. 3a, b) of sediments with refractory elements normalized to the Upper Crust (UC) values [24] they are close to 1, suggesting an upper crustal origin. This is also indicative of the recycling of materials: vulcanites, metamorphites, sedimentites from the Paleozoic, their further denudation, the posterior injection of younger magma in the Mesozoic and Cenozoic, and their subsequent weathering and sedimentation.

Conclusions

As per their spidergrams normalized to PM and UC as well as the calculated correlations, one must conclude that the sediments of two sets of rivers present different *provenance*.

The sediments from the Pilcomayo & Verde Rivers and from the km164-Wetland very certainly evolved as the sub-Andean/Andean metamorphic/sedimentary materials and that those of the Confuso, Aguaray, Negro, Montelindo rivers, did not. The latter represent a relatively ancient system of Passive Continental Margin *provenance.*

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