

SELECTED TRACE AND MINOR ELEMENTS IN ASUNCIÓN SOFT ROCKS

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Geochemical processes in soft immature rocks of the Asunción area are studied through X-ray fluorescence analysis of some trace and minor elements used as provenance indicators. Good correlation between light rare earth elements and other refractories were found and that the analytical data suggest inter alia an overall stable continental area setting.

1 Introduction

The city of Asunción, capital of Paraguay is located between the latitudes 25° 13' 22" S and 25° 22' 03" S and longitudes 51° 31' 38" W and 57° 10' 30" W [1] on the left side of the Paraguay River, in Eastern Paraguay, on the former western margin of Gondwana. The age of its sediments is not well established and they were considered belonging to the upper Triassic [2], Tertiary [3], [4], Cretaceous [5]. The soils still have not been fully studied but *sensu latu* can be considered as red-yellow podzolic [6]. Whilst there are several magmatic rocks plugs of the Tertiary, very few outcrops of soft rocks exist. No hard sedimentary rocks (except in contact zones of magmatic plugs) can be found but widespread "cemented sands" and soft sandstones which constituted the bearing stratum [7] of Asunción.

Under effects of the water table, the levels of which are strongly influenced [8] by the Paraguay River, substratum components can remain imbibed and become very friable. These materials are found from the surface to a depth of around twenty meters.

It is of interest to look for the relationship of such materials with the magmatic events occurred in the area, as well as with the country rocks of the surroundings and elsewhere. This can be achieved using contents of light rare earth elements (LREE) together with other refractory elements, as provenance and geochemical indicators [9], [10].

In this work, using XRF analytical technique, the Rb, Sr, Y, Zr, Nb, Ba, La, Ce and Nd content in the above mentioned materials were investigated. The determination of Ti, Mn and Fe, which are usually correlated with those elements were also performed [11], [12].

2 Experimental

Sample preparation

Two sets of samples were studied: a) taking advantage of selected buildings construction works in the city, seven sampling sites (coordinates of sampling sites: A1: S 25° 16' 36,6" and W 57° 38' 6,6"; A2: S 25° 13' 51,7" and W 57° 34' 41,9"; A3: S 25° 17' 36,2" and W 57° 37' 36,5"; A4: S 25° 16' 44,3" and W 57° 38' 11,1"; A5: S 25° 17' 10,7" and W 57° 36' 59,2"; A6: S 25° 16' 31,3" and W 57° 36' 34,2"; A7: S 25° 14' 40,9" and W 57° 34' 49,0") were chosen and collected materials labeled as A1, A2, A3, etc., respectively. The last four are the typical "cemented sands" (as established under a calibrated microscope), the main component of the bedrock substrate and widespread in all area of Asunción. b) Specimens of sandstones belonging, according the literature, to the geological periods above mentioned and to the Permian, were collected at localities of Yeguahaty (A8), Ypané (A9-A10), San Ignacio (A11) and Santa Rosa (A12) (coordinates of sample sites: A8: S 22° 56' 38,5" and W 56° 44' 05"; A9: S 25° 27' 30" and W 57° 30' 47"; A10: S 26° 53' 12" and W 57° 01' 35"; A11: S 26° 52' 55" and W 56° 49' 40").

The samples were dried, then ground and sieved for XRF measurements. The powdered samples were pressed into pellets of area weight $\sim 0.1 \text{ g cm}^{-2}$.

XRF measurements and analysis

The XRF measurements and quantification were performed utilizing the facilities of the XRF laboratory at "Jožef Stefan" Institute in Ljubljana, Slovenia.

For the excitation of fluorescence radiation the radioisotope sources of ^{109}Cd (20 mCi), ^{55}Fe (20 mCi) and ^{241}Am (50 mCi) were utilized. The energy dispersive X-ray spectrometer was based on a Si(Li) semiconductor detector (FWHM $\approx 140 \text{ eV}$ at 5.9 keV). The analyses of complex spectra were performed by AXIL [13] software, which is based on iterative non linear least square fit of the spectra by 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 Kump [14]. This software utilizes the so-called transmission-emission method for determination of the absorption in the sample and then finds the solution of the system of basic XRF equations by iteration. The basic XRF equations (one equation for each measured element) relate 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 all measured and unmeasured elements, 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

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

3 Results and Discussion

The average of absolute values of Rb, Sr, Y, Zr, Nb, Ba, La, Ce and Nd occurrence in the Asunción sedimentary material are shown in Table 1a. Those for minor elements Ti, Mn, Fe are given in Table 1b.

The values of trace elements are lower than those found in sediments of Itaipú Dam [15]; the latter on tholeiitic basalt bed (Alto Paraná Formation), the former in the Asunción area of alkaline magmatism.

In the Eastern Paraguay, postpaleozoic magmatism is exposed in the Cretaceous by the extended lava flow of the Alto Paraná Formation-Serra Geral (137-127 Ma), represented by tholeiitic basalts [16], [17] which are widespread through the country, but concentrated in the east, and also by alkaline potassic rocks (132-118 Ma) found in Asunción-Sapucaí Graben [18], [19]. Tertiary magmatism (61-39 Ma), of sodic alkaline rocks is concentrated in the Asunción region: nefelinites, phonolites, etc. outcrop in different bodies [20], [21]. Most of these samples, usually under the water table, are friable and easily disaggregated, when still imbibed with water. But after a few hours in a dry environment, they become harder, more rock-like; this is more apparent in samples more clayed and exhibit a content of the fine matrix, over 50 % (A1) and 25-30 % (A2): this is similar to the behavior of plinthite: on drying, it changes to plinthitstone and finally to ironstone.

Table 1a. Concentration ($\mu\text{g g}^{-1}$) of trace elements in the Asunción region

	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇
Rb	27.1 ± 3	38.5 ± 4.5	9.5 ± 1.2	32.6 ± 3.8	22.1 ± 2.6	31.5 ± 3.7	33.1 ± 3.9
Sr	607 ± 63.9	151 ± 17.6	7.2 ± 0.9	22.7 ± 2.7	15.7 ± 1.9	23.6 ± 2.8	26.9 ± 3.2
Y	7.6 ± ND	10.9 ± 1.3	27.5 ± 3.2	7.83 ± 0.95	10.2 ± 1.22	6.4 ± 0.79	6.6 ± 0.8
Zr	228 ± 24.0	142 ± 16.6	78.9 ± 9.2	163 ± 19.0	139 ± 16.2	100 ± 11.7	128 ± 14.9
Nb	100 ± 10	28.9 ± 3.4	1.67 ± 0.8	3.4 ± 0.46	3.30 ± 0.4	3.21 ± 0.4	3.49 ± 0.5
Ba	667 ± 69	385 ± 40.6	111 ± 11.8	187 ± 19.7	133 ± 14.1	182 ± 19.2	173 ± 18.3
La	69.5 ± 7.7	29.5 ± 3.3	16.4 ± 2.1	11.6 ± 1.6	15 ± 1.9	14.5 ± 1.7	13.6 ± 1.7
Ce	107 ± 11.5	62.8 ± 6.7	23.7 ± 2.8	21.7 ± 2.6	23.5 ± 2.7	23.7 ± 2.6	30.9 ± 3.4
Nd	28.5 ± 4.5	22.8 ± 2.8	31 ± 3.7	14.1 ± 2.2	18.1 ± 2.5	12 ± 1.6	15.6 ± 2.1

Table 1b. Concentration (mg g^{-1}) of minor elements in the Asunción region

	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇
Ti	14.5 ± 1.52	3.45 ± 0.4	0.76 ± 0.1	0.98 ± 0.1	1.02 ± 0.1	1.07 ± 0.1	1.03 ± 0.1
Mn	0.34 ± 0.05	0.62 ± 0.08	0.08 ± 0.01	0.08 ± 0.01	0.09 ± 0.02	0.69 ± 0.01	0.09 ± 0.01
Fe	76.4 ± 8.02	20.4 ± 2.4	128 ± 14.9	6.24 ± 0.8	4.96 ± 0.6	5.95 ± 0.7	6.67 ± 0.8

The system $Fe^{2+} \leftrightarrow Fe^{3+} + 1 e^-$ plays an important role. Most of iron in magma is present as Fe^{2+} ; but according the redox gradient of the environment, precipitates as Fe^{3+} , usually goethite-lepidocrocite ($\alpha\text{-FeOOH}$), major constituent of Phanerozoic plinthite-stone. Poorly crystalline, they are metastable (~ 9 kJ) with respect of hematite (Fe_2O_3) [22], stable, with greater crystal energy. Formations of these oxides/hydroxides have hydrothermal origin [23]. Redox gradient develops where oxidizing and reducing fluids meet [24].

Reduced conditions mobilized the Fe and Mn [25] and iron compounds are dissolved. In accordance with gradient, this process repeats. The water enriched thus with iron (A3 sample) ascends in vertical joints up to where Fe_2O_3/Fe_3O_4 crystallized and forms iron-stone.

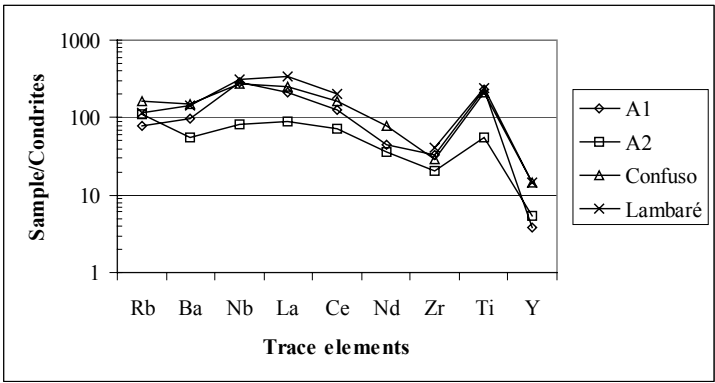


Fig. 1a. Chondrite-normalized values trace elements diagram for A1, A2, and from reference [29] data, for Confuso dyke and Lambaré plugs.

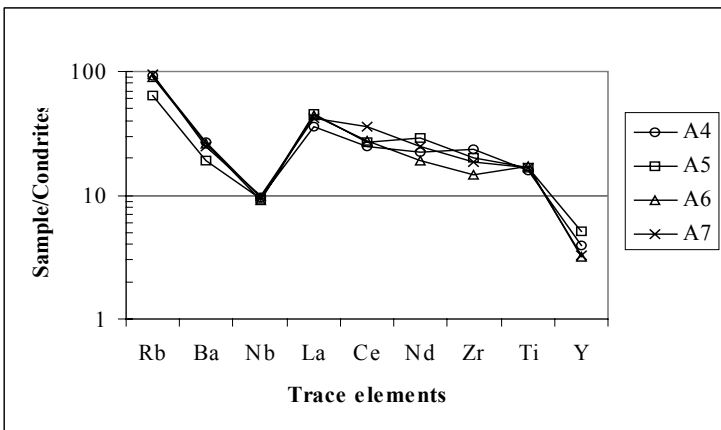


Fig. 1b. Chondrite-normalized values trace elements diagram for immature sandstones from Asunción.

Iron oxyhydroxides absorb trace metals in sediments. Therefore, the correlation factors with 95 % of confidence were calculated. The results for the immature materials are as follows: La-Fe: $r = 0.995$; Ce-Fe: $r = 0.964$; Nd-Fe: $r = 0.881$; Zr-Fe: $r = 0.879$; Nb-Fe: $r = 0.998$ and Ti-Fe: $r = 0.999$, probably iron-titanate. On the other hand no correlations of these elements in the hard rocks exist.

Magma 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 [26].

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 concentrate in the melt. Thus, when a portion of mantle, known to be similar in composition to chondrites [27], [28], forms basaltic melt, such elements become enriched in the liquid phase, and the solid peridotite stays depleted in REE.

Zirconium originates accessory minerals, which occurred in igneous rocks. They are refractories and very stable. Positive correlations were found between Zr and other incompatible elements: La – Zr: $r = 0.851$; Ce – Zr: $r = 0.811$; Nd – Zr: $r = 0.811$; Nb – Zr: $r = 0.879$ and Ti – Zr: $r = 0.879$. In addition, strong correlation of these elements are found in the hard rocks samples, except for Zr – Fe ($r = -0.111$).

Also Ti vs incompatible elements shows strong correlations as follows: La-Ti: $r = 0.993$; Ce-Ti: $r = 0.957$; Nd-Ti: $r = 0.875$; Nb – Ti: $r = 0.996$, etc.

Comparison among REE and other refractory elements can be done by normalizing the analysis to a reference standard, in this work chondrites [9]. Thus, Fig. 1a shows the spidergram of incompatible analyzed elements (Sr is not included) of samples A1 and A2 together with those magmatic bodies from Confuso (phonolitic dyke) and Lambaré (nephelinite plug), included for comparison (data taken from reference [29]). The strong influence of Tertiary magmatic activity is apparent.

The nephelinites reflect the composition of primary magma of the mantle, in this case garnet peridotite sources [21], different from sources of alkaline-Cretaceous magmatism. The spidergram shows positive spikes on Nb typical of tertiary magmatic rocks [19].

On the other hand, samples A4, A5, A6, A7, “immature” sandstone, present a strong negative anomaly of Nb, and Ti depletion very close to the alkaline-Cretaceous igneous materials, as can be in the same way seen in Fig. 1b.

It is very interesting to compare the analysis of these values with those of “mature” sandstones as presented in Tables 2A and 2B and (Sr excluded) in their spidergrams (Fig. 2).

Samples from Misiones Formation (A11, A12) and Patiño Formation (A9, A10) have the same patterns as well as chondrite-normalized values, suggesting the same magmatic provenance.

However, A8 samples average, taken in a upper Carboniferous-Permian area [4], follows the same signature although, it has higher absolute values, a stronger Nb negative anomaly and pronounced Ba depletion; they are more like the “immature” sandstone of the Asunción region (see Fig. 1b).

Table 2a. Concentration ($\mu\text{g g}^{-1}$) of trace elements in hard sedimentary rocks

	A ₈	A ₉	A ₁₀	A ₁₁	A ₁₂
Rb	44.9 ± 5.3	5.29 ± 0.83	2.83 ± 0.8	3.3 ± 0.8	1.94 ± 0.7
Sr	83.2 ± 9.7	8.05 ± 0.81	4.63 ± 0.6	16.1 ± 1.57	34.6 ± 2.96
Y	22.8 ± 2.7	2.2 ± 0.42	1.9 ± 0.44	4.13 ± 0.66	2.32 ± 0.55
Zr	343 ± 40	72.1 ± 5.7	55.8 ± 4.44	81.3 ± 6.46	126 ± 9.97
Nb	4.39 ± 0.55	1.9 ± 0.34	2.06 ± 0.42	3.04 ± 0.54	1.99 ± 0.48
Ba	418 ± 44	18.2 ± 1.4	45.8 ± 2.79	66.5 ± 3.97	28 ± 1.72
La	20.6 ± 2.3	8.45 ± 1.0	6.52 ± 0.6	7.84 ± 0.53	8.36 ± 0.62
Ce	47.4 ± 5.1	10.7 ± 1.2	6.96 ± 0.68	15.1 ± 0.94	14.3 ± 0.95
Nd	24.4 ± 2.9	3.07 ± 0.85	4.52 ± 0.75	4.79 ± 0.95	7.72 ± 0.72

Table 2b. Concentration (mg g^{-1}) of minor elements in hard sedimentary rocks

	A ₈	A ₉	A ₁₀	A ₁₁	A ₁₂
Ti	2.53 ± 0.3	0.39 ± 0.037	0.29 ± 0.029	0.82 ± 0.13	1.11 ± 0.08
Mn	0.078 ± 0.01	0.16 ± 0.025	0.15 ± 0.025	0.38 ± 0.04	0.2 ± 0.03
Fe	5.13 ± 0.6	2.81 ± 0.2	2.38 ± 0.19	18 ± 1.42	5.7 ± 0.45

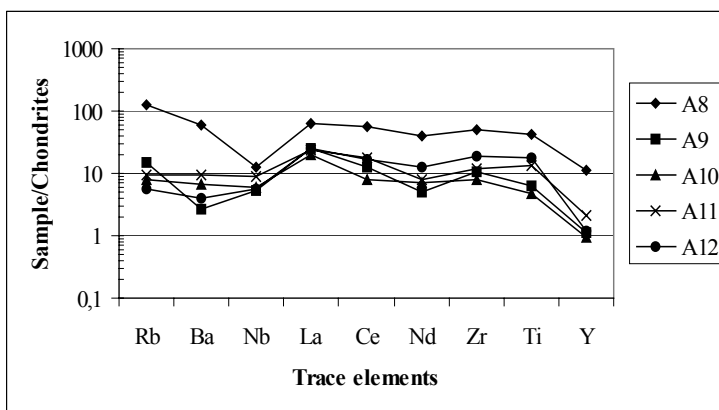


Fig.. 2. Chondrites-normalized values trace elements diagram for mature sandstones from Jeguahaty, Ypané, San Ignacio and Santa Rosa.

In spidergrams of both Asunción soft rocks and mature sandstone samples there are some indicators typical of intracratonic deposit: Zr spike correlating with the presence of heavy minerals in the source; negative anomaly in Ti; as well as a strong negative anomaly of Sr (inferred from the data Table 1B). Intracratonic/passive margin environment usually has anomalies <1 for these elements.

On the other hand, positive Ti anomaly tends to indicate, as demonstrated in Fig. 1a, input similar to a typical of active continental area margin [30], [31]. This is in accord with the active effect on samples A1 and A2 of the above mentioned Tertiary magmatism.

The low values of Y in the samples reflect the strong fractionation of heavy REE (HREE).

4 Conclusions

The analysis of the incompatible elements contents in the widespread typical immature sandstone of Asunción region, rather than Tertiary, suggest a Cretaceous or elder signature; further studies are necessary.

In addition, the deposition and metadiagenesis of the immature soft rocks as well as mature sandstones occurred as processes of intracratonic settings. On the other hand, only in few vertical joints, strong influence of Tertiary magmatism can be observed.

The close values and patterns, in the Misiones and Patiño Formation samples, of incompatible elements, are for both indicators of the same source provenance.

References

- [1] DIGM: Carta de Asunción, Informe Planimétrico sobre fotografías aéreas del año 1984, 5370 II (1985).
- [2] Harrington H.: Fac. Ci. Ex. Fis. Mat., Cont. Cient., Ser. E., *Geología I* (1950) Buenos Aires, Argentina.
- [3] Mapa Geológico del Paraguay y Memoria Explicativa. UNDP Proyect PAR 83/005 (1986).
- [4] Fúlfaro V. J.: *In: Alkaline Magmatism in Central-Eastern Paraguay.* (Comin-Chiaramonti P. and Gomes C.Eds.) Universidad de S. Paulo Editora Sao Paulo, Brasil (1995) p. 17.
- [5] Bartel W.: *In: Primer Congreso Paraguayo de Geotécnica,* Asunción, Paraguay (1997) 275.
- [6] González E. E.: Personal communication (2005).
- [7] Bosio J. J.: *In: 12th Panamerican Conference on Soil Mechanics and Geotechnical Engineering.* M.I.T. Cambridge, Ma., USA (2003).
- [8] Facetti F. S. and Facetti J. F.: Unpublished data.
- [9] Bonin B.: *Magmatisme et Roches Magmatiques,* Dunod, Paris (2004).
- [10] Petersen N., Smith P., Mortensen J., Creaser R. and Tipper H.: *Can. J. Earth Sci.* 41 (2004) 103.
- [11] Rankama K. and Sahama Th. *Geoquímica* (Trad. Castellana) Aguilar Ed. Madrid, España (1959).
- [12] Albarède F.: *Geochemistry.* Cambridge University Press, Cambridge, UK (2004).
- [13] Van Espen P., Nullens H., and Adams F.: *Nucl. Instrum. Meth.* 142 (1977) 243.
- [14] Kump P.: *QAES Instruction Manual* (1988).
- [15] Facetti J. F., Kump P. and Díaz Z.: *Czech J. of Physics* 53 (2003) A209.
- [16] Melfi A., Piccirillo E. and Nardy A.: *In: The Mesozoic flood volcanism of the Paraná Basin petrogenetic and geophysical aspects,* Piccirillo E. M., Melfi A.J., Eds. Instituto Astronómico e Geofísico University of Sao Paulo, Brasil (1988) 1.
- [17] Piccirillo E. M et al.: *Rev. Geoch. Bras.* 1 (1987) 53.

- [18] Gomes C. B., Comin-Chiaramonti P., Velázquez V. F. and Orué D.: *In: Alkaline magmatism in Central-Esastern Paraguay* (Comin-Chiaramonti P. and Gomes C. Eds.) Universidad de S. Paulo Editora Sao Paulo, Brasil (1995) 31.
- [19] Comin-Chiaramonti P. et al.: *In: Alkaline magmatism in Central-Esastern Paraguay* (Comin-Chiaramonti P. and Gomes C. Eds.) Universidad de S. Paulo Editora Sao Paulo, Brasil (1995) 123.
- [20] Bitschene P.R.: *Mesozoischer und Kanozoischer anorogener magmatismus in OstParaguay*, Doctoral Dissertation accepted by Heidelberg University, 1987.
- [21] Comin-Chiaramonti P. et al.: *Eur. J. Mineral.* 3 (1991) 507.
- [22] Majzla J., Bender Koch C. and Navrotsky A.: *J. Goldschmidt Conference Abstract* (2002) A 477.
- [23] Menuge J. F. et al.: *J. Goldschmidt Conference Abstract* (2002) A 507.
- [24] Breit G.: *The Geological Society of America Annual Meeting*, Sesion No. 118-0 (2001).
- [25] Walton-Day K.: *The Geological Society of America Annual Meeting* Sesion No. 118-0 (2001).
- [26] Cornell D.: *Pure and Applied Chemistry* 65 (1993) 2453
- [27] Schmitt R. A., Smith R. H. and Lasch J. E.: *Geochem. Cosmochem. Acta* 27 (1963) 577.
- [28] Haskin L. et al.: *In: Physics and Chemistry of the Earth*, Ahrens L. H. Press F., Runcom S. and Urey H. C. Eds., Pergamon Press, Oxford (1966).
- [29] Comin-Chiaramonti P. et al.: *In: Alkaline Magmatism in Central-Eastern Paraguay* (Comin-Chiaramonti P. and Gomes C. Eds.) Universidad de S. Paulo Editora Sao Paulo, Brasil (1995) 123.
- [30] Roser B. P. and Korsch R. J.: *Chemical Geology* 67 (1988) 119.
- [31] Burnett D. J. and Kuirk D. G.: *J. Geol. Soc.* 158 (2001) 913.