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Statistic behavior of major and minor elements in basic, intermediate and acidic rocks of the Serra Geral Formation and Arapey Group, Paraná Large Igneous Province, South America

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Abstract-The evolutionary processes of the South American portion of the Paraná-Etendeka Province, composed of the Serra Geral Formation (Brazil, Argentina and Paraguay) and Arapey Group (Uruguay) had been developed in 1.2 Ma with a climax located of 134.7 Ma, giving rise to extrusive rocks (flows) and intrusive rocks (dykes and sills) of composition ranging from basalts to rhyolites. In the last four decades, many authors have produced geochemical data sets on these rocks, which were published or remain unpublished. The compilation of these data sets and its standardization from the geochemical and geographic viewpoints, gave rise to a database containing analysis of SiO_2, TiO_2, Al_2O_3, FeO_{total}, MnO, CaO, Na_2O, K_2O, P_2O_5, Ba, Ce, Cr, La, Ni, Rb, Sr, Zr, and Y from 4,257 outcrop and subsurface (core) samples. In this article we present the techniques used for the construction and standardization of the database and the statistical analysis of the geochemical data. The application of statistical techniques, especially the modeling of probability plots, showed that most variables are polymodal, which, from the statistical point of view, means the existence of different populations and, from the geological and geochemical points of view, suggest a complex combination of processes of generation, mixing, contamination and differentiation. These data gave rise to statistical reference levels for the set of basic , intermediate and acid rocks of Paraná LIP. The results indicate thus the need for geochemical studies considering a prior stratification of data by referencing the thresholds of populations for each variable. The authors also suggested some simple rules for publishing geochemical data in order to facilitate its aggregation to the database.
Keywords: Paraná LIP, Serra Geral Formation, Arapey Group, geochemistry, statistical modeling, probability plots.

Resumo - COMPORTAMENTO ESTATÍSTICO DOS ELEMENTOS MAIORES E MENORES EM ROCHAS BÁSICAS, INTERMEDIÁRIAS E ÁCIDAS DA FORMAÇÃO SERRA GERAL E GRUPO ARAPEY, *PARANÁ LARGE IGNEOUS PROVINCE*, AMÉRICA DO SUL. Os processos evolutivos da porção sulamericana da Província Paraná-Etendeka, composta pela Formação Serra Geral (Brasil, Argentina e Paraguay) e Grupo Arapey (Uruguay) se desenvolveram em 1,2 Ma com clímax localizado em 134,7 Ma, dando origem a rochas extrusivas (derrames) e intrusivas (diques e soleiras) de composição que varia desde basaltos até riolitos. Nas últimas quatro décadas, muitos autores produziram conjuntos de dados geoquímicos sobre essas rochas, que foram publicados ou permaneceram inéditos. A compilação desses conjuntos de dados e sua padronização sob os pontos de vista geoquímico e geográfico deu origem a uma base de dados que contém análises de SiO_2, TiO_2, Al_2O_3, FeO_{total}, MnO, CaO, Na_2O, K_2O, P_2O_5, Ba, Ce, Cr, La, Ni, Rb, Sr, Zr, e Y realizadas em 4.257 amostras de rocha provenientes de afloramentos e testemunhos de sondagem. No presente artigo são apresentadas as técnicas de construção e padronização dessa base de dados, assim como o tratamento estatístico das variáveis analíticas. A aplicação de técnicas estatísticas, especialmente a modelagem dos gráficos de probabilidade, evidenciou que a maioria das variáveis analisadas é polimodal o que, sob o ponto de vista estatístico, significa a existência de diversas sub-populações e, sob os pontos de vista geológico e geoquímico, sugere uma combinação complexa de processos de geração, mistura, contaminação e diferenciação. Esse tratamento estatístico deu origem a níveis de referência particulares para o conjunto de rochas básicas, intermediárias e ácidas da LIP Paraná. Os resultados obtidos indicam assim, a necessidade de que estudos geoquímicos considerem uma estratificação prévia dos dados, usando como referência os limiares das populações de cada variável. São também sugeridas algumas regras simples para que dados geoquímicos futuramente produzidos possam ser agregados a essa base de dados.
Palavras chave: Paraná LIP, Formação Serra Geral, Grupo Arapey, geoquímica, modelagem estatística, gráficos de probabilidade.

1.Introduction

The geological mapping of large igneous provinces, mainly those of continental basalts, involves the processing of geochemical data in order to reconstitute the processes responsible for the magma generation and differentiation during evolution of each province or region. In order to provide robustness to the statistical processing, to the data modeling and especially to the spatial distribution and the geochemical stratigraphy, it is necessary to count on a reliable database. The Paraná Large Igneous Provice (Paraná LIP) covers part of four South American countries: Brazil, Argentina, Paraguay and Uruguay and extends for approximately 1,000,000 Km^2 (Fig. 1). The deepest flow, and probably the first, is located at 1,666 m below sea level (Piccirillo & Melfi, 1988) and the highest one at 1,832 m above sea level (Mincato, 2000). The deepest sill occurs at 4,083 m below sea level (Regelous, 1993).

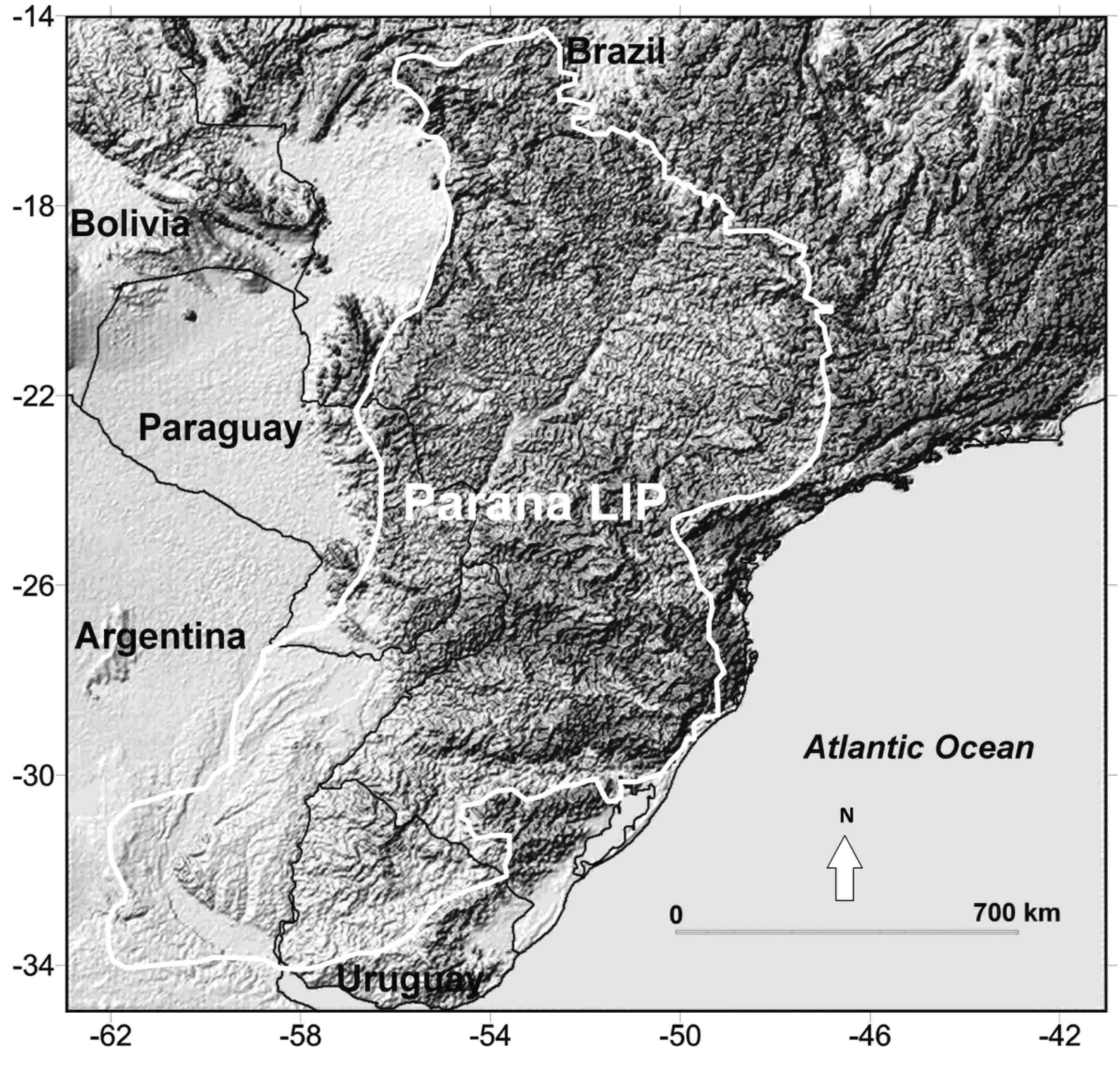


Figure 1. Boundaries of the Paraná LIP (Peate *et al.*, 1992) over the digital elevation model from SRTM and ASTER radar data.

This huge magmatic system, that includes intrusive (dykes and sills) and extrusive (flows) rocks, was active in Cretaceous times from approximately 1.2 Ma, with its climax around 134.7 Ma (Thiede & Vasconcelos, 2008, 2010). The igneous rocks of Paraná LIP receive different denominations: Serra Geral Formation in Brazil, Argentina and Paraguay, and Arapey Group in Uruguay.

Geochemical data from local to regional coverage have been presented in many articles, dissertations, thesis and books on the geochemistry of the igneous rocks that constitute the Paraná LIP. A compilation was presented by Rüegg (1975) to which a new data set was aggregated, based on the chemical analysis of oxides and minor elements from 135 rock samples. The spatial distribution of geochemical values was obtained from trend surface analysis. Rüegg (1975) also conducted a multivariate characterization of the spatial distribution of geochemical values through factor analysis, the same approach taken by Macedo & Rüegg (1974). A database of complete analysis of major (oxides) and minor elements was produced by the research team coordinated by Piccirillo & Melfi (1988) from 1,477 drill core and outcrop rock samples encompassing the entire Serra Geral Formation (Arapey Group). Large amounts of regional to local data on the Paraná LIP have been published by different authors. The present article describes the recompilation of such datasets into a single database that was standardized to the best possible use of the scattered geochemical information and sample location available. The work involved several review steps in order to identify and correct data discrepancies, eliminate redundancy, and ensure consistency. As a result, a consolidated database of reliable analytical results for SiO_2, TiO_2, Al_2O_3, FeO_{total}, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, Ba, Ce, Cr, La, Ni, Rb, Sr, Zr, and Y, from as many as 4,257 scattered surface and subsurface samples of basic, intermediate and acidic intrusive and extrusive rocks was built covering of the entire Paraná LIP.

The purposes of this paper are: (a) to present the statistical estimators of major and minor elements, (b) to establish reliable reference values for the major and minor elements in the Paraná LIP, (c) to identify new population thresholds for all major elements considered in petrological modeling, (d) to present the methodology and procedures followed for data compilation and review that allowed a robust and consistent geochemical database to be built for the Paraná LIP. Thus, the present paper does not address petrogenetic interpretation of the major and minor elements distribution, but only the description of their statistical patterns as a consistent framework for further studies.

The significance of the major and minor elements polymodality

The differentiation of basaltic magmas generated by partial melting of the upper mantle or the base of the crust produces intermediate and silica rich magmas under the effect of combined processes: crystal fractionation, magma mixing, crustal contamination and partial melting of the crust induced by the presence of primary magma (Bryan *et al.,* 2002). Hildreth & Moorbath (1988) characterize this set of processes such as *MASH* (mixing, assimilation, storage and homogenization). In tabular and subhorizontal intrusive bodies (sills) it is possible that have happened cumulatic processes that may cause the concentration of some elements in its basal portion such as MgO, FeO_{total}, CaO, Cr and Ni. The complexity of the igneous processes and the interaction of the magma with crustal rocks and geofluids during its rising to surface produces also a complex statistical behavior of the major and minor elements. This confronts the concept of bimodality for the Paraná LIP. The authors of the present article believe that such bimodality is artificial and it was induced by the small number of samples used in former statistical analyses.

The presence of multiple sub-populations (*polymodality*) in a geochemical data set reflects the complexity of the geological and geochemical processes involved. Therefore, geochemical data sets, especially those representing large and complex areas like the Paraná LIP, have many subpopulations mixed in the values of each element. Sinclair (1974, 1976) showed that curved patterns in a probability plot characterize the presence of two or more mixed populations. The proportion of each population in the mixture is given by particular inflection points on the cumulative frequency curve. These proportions are used to isolate each population from the mixture. The procedure of breaking down a complex cumulative frequency curve into its component sub-populations and obtaining statistical estimates from it is named *partitioning of probability graphs*. Mixed subpopulations must be examined in detail because of the likelihood that each statistical sub-population represents a distinct geochemical environment, a possibility that is commonly ignored in practice (Sinclair & Blackwell, 2006). Thus, when dealing with geochemical data sets, it is important to identify and circumscribe homogeneous environments represented by sub-populations (sub-sets) which can be observed, isolated and characterized by means of probability modeling graphs following the procedure explained by Sinclair (1974, 1976) and Sinclair & Blackwell (2006).

Some terms like sample and population have different meanings in geochemistry and statistics. So, for a better understanding and clarity, in this article they should be understood as follows:

Population – the set of all values, including those actually observed and also those potentially observable. In the present case, the term population refers to the Paraná LIP as a whole;

Statistical sample – a representative data set collected from the population. In the present case the term refers to the compiled geochemical database;

Sub-population – a sub-set of the statistical sample. In the present case it refers to each data sub-set achieved by probability plot modeling;

Geochemical sample – a representative portion of rock collected from an outcrop or a drill hole.

The findings presented here can be the basis for further research on the relationships between major and minor elements or their specific ratios and functions in order to contribute and improve the stratigraphic and petrogenetic interpretations of the Paraná LIP.

2. Materials and methods

2.1. Geographical distribution of the database

The data sets were obtained from 4,257 geochemical samples which are distributed by the whole Paraná LIP, with a lower data density in the NW and SW portions of the province. Most of them (3,678 geochemical samples or 86.40%) were collected from outcrops (Fig. 2).

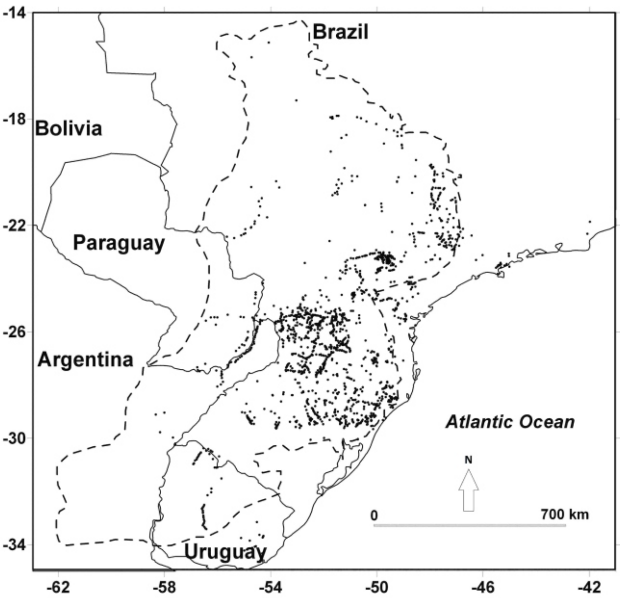


Figure 2. Location map of the outcrop geochemical samples stored in the database.

The number and distribution of geochemical data in 579 geochemical samples (13.60% of the database) is remarkable, since they were collected from either continuous cores of petroleum exploration drill holes or chip samples from underground water production wells. From this total, 266 came from only eight drill holes in Brazil (from the states of São Paulo, Paraná and Santa Catarina), collected as composite geochemical samples that represent intervals as long as e.g. 10 meters of drill cores. The other 313 geochemical samples were collected from more than 22 vertical drill holes – some identified, others not – that were distributed from the state of São Paulo through of Uruguay and spaced by tenths or thousands meters down the holes, or even as a single sample from a deep drill hole (Fig. 3).

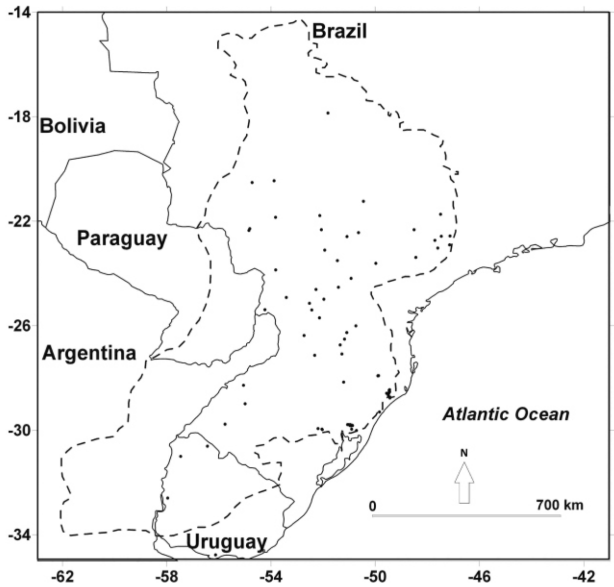


Figure 3. Location map of the vertical drill holes containing at least one geochemical sample stored in the database.

2.2. Methods

Two aspects were considered fundamental in the process of review, consistency check and integration of the geochemical data base: the degree of standardization of the analytical results and the homogeneity of their spatial positioning. Additionally, valuable information like the source of the geochemical sample (outcrop or drill core), the kind of emplacement (intrusive or extrusive) and the type of occurrence (dyke, sill or flow) was added to the database. It should be stressed that the original data sources were constructed in accordance with many different concepts and references, such as geographic and projected coordinates and vertical datum. Also, such data were presented either in the original format or recalculated to 100% on an anhydrous base**.** Recalculations of Fe_2O_3 and FeO from the original FeO_{total} as received from the laboratory were also presented. All these variables were considered in the process of standardization.

The data sets were compiled from the following sources, presented in chronological order:

De La Roche *et al.* (1974, *apud* Bossi & Schilipov, 2007), Rüegg (1975), Bellieni *et al.* (1983), Marimon *et al.* (1983), Bellieni *et al.* (1984a), Fodor *et al.* (1985), Mantovani *et al.* (1985), Petrini *et al.* (1987), Bertrand (1988, *apud* Bossi & Schilipov, 2007), Bossi & Navarro (1988), Peate *et al.* (1988), Picirillo & Melfi (1988), Piccirillo *et al.* (1988), Piccirillo *et al.* (1989), Roisenberg (1989), Peate (1989), Campanha (1991), Chies (1991), Whittingham (1991), Viero (1992), Regelous (1993), Garland *et al.* (1995), Nardy (1996), Peate & Hawkesworth (1996), Renne *et al.* (1996), Rifas Gómez & Maquelín (1996, *apud* Bossi & Schilipov, 2007), Turner *et al.* (1996), Maniesi & Oliveira (1997), Licht & Arioli (1998), Feraud *et al.* (1999, *apud* Bossi & Schilipov, 2007), Peate *et al.* (1988), Peate *et al.* (1999), Turner *et al.* (1999), Kirstein *et al.* (2000), Mincato (2000), Romanini & Albuquerque (2000), Vanzela *et al.* (2004), JICA (2005), Machado (2005), Petersohn (2006), Wildner *et al.* (2006), Lopes (2008), Nardy *et al.* (2008), Torres *et al.* (2008) and Machado (2009). Few unpublished data produced by the authors or other researchers cited in the references were also used in the database compilation.

Data sources indicate that the main analytical technique used for the determination of major elements (SiO_2, TiO_2, Al_2O_3, FeO_{total}, MnO, MgO, CaO, Na_2O, K_2O and P_2O_5) was the X-ray fluorescence and for the minor elements (Ba, Ce, Cr, La, Ni, Rb, Sr, Zr and Y), were used X-ray fluorescence, atomic absorption spectrometry, ICP-OES, ICP-MS and neutron activation.

All data treatment and modeling was performed using the oxides values recalculated to 100% on an anhydrous base. The variation in LOI (loss on ignition) values may reflect the combination of processes such as: (a) contact between the magma and crustal fluids during its ascension, (b) hydrotermalism due to late migration of crustal and/or juvenile fluids (c) samples collected from base, core and top of the A'a and pahoehoe flows, (d) contemporary and/or late weathering. The data sources do not contain any information that allows an appreciation of this subject.

The step-by-step of the methodology adopted to standardize, criticize and give consistency to the database can be found in Appendix 1.

2.2.1. Statistical data analysis

The statistical diagnosis and modeling of the major and minor elements were performed considering the whole database. The histograms and probability plots were built in class intervals of 0.1 standard deviations, which give a specific number of class intervals for each element. The *x* axis, showing the major and minor elements contents, remains constant for the histograms of each variable. The *y* axis of the histograms shows their relative (percentage) frequency. This allows comparisons between the whole dataset and some specific strata of the variable. The statistical analysis, estimates, and histograms were performed using the Statistica software package (StatSoft, 2008).

2.2.2. Isolating populations by probability plot modeling

In order to test the 20 geochemical variables – major and minor elements – regarding polymodality and to isolate and characterize sub-populations, the cumulative frequency curves and probability graphs were analyzed with the P-REZ software package (Bentzen & Sinclair 2002) following the technique presented by Sinclair (1974, 1976). But since P-REZ modeling is limited to eight sub-populations, a two-step modeling procedure had to be adopted for all variables. For those showing a clear histogram gap, e.g. SiO_2, the midpoint of the lower frequency class interval was adopted as a cut-off, separating low from high values. For those variables not showing a histogram gap, e.g. Al_2O_3, the following procedure was adopted. Firstly, using all data, the extreme sub-populations were isolated and characterized, the sub-population with the higher proportion in the data set being identified. Secondly, the modeling was performed by using only data from the sub-population identified in the first step so as to try and isolate underlying sub-populations. The results of both steps were condensed into a single table.

To avoid the superposition of the ends of neighboring sub-populations, P-REZ cuts each one by using the thresholds placed in mean - 2 standard deviation for the higher sub-population and mean + 2 standard deviations for the lower sub-population. In this manner, the fields of existence of each sub-population became restricted between 2% and 98% of the probability scale.

Because of their extremely asymmetric distributions, some variables had their probability plots expressed in log scales so that they could be modeled. In such cases, the final threshold or sub-population estimates are expressed in the original units (% or ppm), exception being made for the standard deviation. The final results for each variable, i.e. their absolute and relative frequencies, statistical estimates and thresholds for each sub-population are summarized in appendix 3 to 6.

It must be stressed that the relative frequency figures do not imply a volume estimate for each group or strata in the Paraná LIP. They refer only to the whole number of geochemical samples for each strata or group.

3. Results and discussion on statistical characterization of the elements

It is important to emphasize that the results achieved with the statistical analysis of SiO_2, TiO_2 and MgO based on the probability plots are quite different from those that have been used and adopted for the Paraná LIP. These new values were based on a robust database, whilst the former values are based on a small amount of samples or imported from other large igneous provinces.

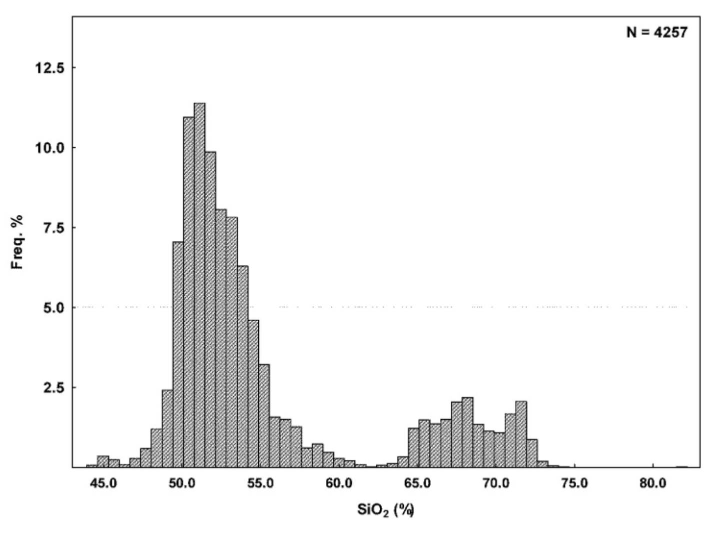
Even considering the representativeness of the database, the values (Appendix 2) and thresholds must be considered as exclusive for the Serra Geral Formation – Arapey Group, and should not be applied directly to other LIPs. These particular and exclusive limits and thresholds constitute the grounds for a new geochemical subdivision of the Paraná LIP that will be proposed in the future, that will characterize not only the magma types, but also the differentiation and crustal contamination processes that the magmas underwent during the evolution of the Serra Geral Formation and the Arapey Group.

The descriptions that follow are concise, both for brevity and the self-explanatory nature of the diagrams, and to briefly characterize the statistical distribution of major and minor elements, exception made for the oxides traditionally used in modeling petrogenetic processes.

3.1. SiO_2

The values for SiO_2 range from 43.95 to 82.17%, encompassing many rock types, from cumulates in basic sills to rhyolite and probably hyper-siliceous inter-trapp sandstone or peperite in one case. The histogram (Fig. 4) reveals the presence of two main groups of values, separated by a region of low frequencies. Bellieni *et al.* (1986) identified this region as situated between 54% and 63% SiO_2 by giving it the name of *silica gap*. According to those authors, the importance of this gap is the role it plays as a threshold separating the basic rocks from the acidic ones, thus characterizing a bimodal igneous activity in the Paraná LIP. Peate (1989) stated that regarding the SiO_2 values, the products of the magmatic events of the Paraná LIP show a marked bimodal distribution and that they could be generally thought as "basaltic" (< 60 wt% SiO_2) or "acidic" (> 60 wt% SiO_2).

From figure 4, it is noteworthy that the low frequency values are located in the central region, but it is also clear that the apparent bimodality does not resist closer examination of the statistical distribution of values as there are at least four modes at approximately 45 %, 53 %, 67 %, and 72 %, which suggests polymodal behavior for the SiO_2 data.



Class n°	Class interval (SiO_2%)	N	Relative frequency (%)
23	58.893 < x <= 59.588	22	0.516
24	59.588 < x <= 60.283	12	0.281
25	60.283 < x <= 60.978	10	0.234
26	60.978 < x <= 61.673	4	0.093
27	***61.673 < x <= 62.368***	1	0.023
28	62.368 < x <= 63.063	3	0.070
29	63.063 < x <= 63.758	5	0.117
30	63.758 < x <= 64.452	16	0.375
31	64.452 < x <= 65.147	54	1.268

Figure 4. Histogram and part of the SiO_2 frequency table in the Paraná LIP emphasizing (in bold italic) the class interval containing the silica gap.

The silica gap actually occurs in the class interval delimited by 61.67 to 62.36 % SiO_2, so the mid-point of this interval (62.02 % SiO_2) was adopted as cut-off. The group of contents lower than the cut-off value was named *low SiO_2* and the higher *high SiO_2* (Fig. 5).

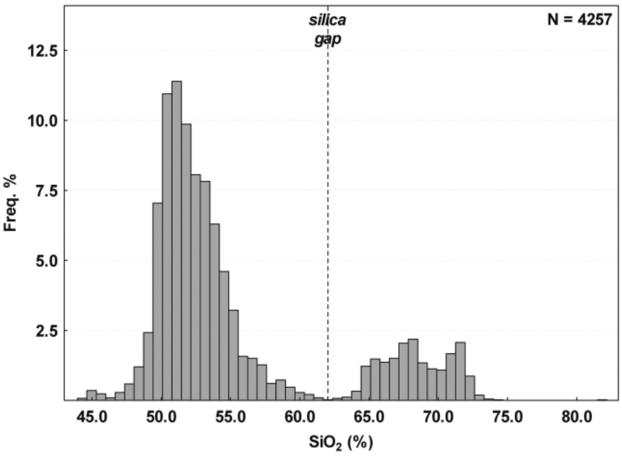


Figure 5. Histogram for SiO_2 showing the *silica gap.*

The contrast between some statistical estimates of the two SiO_2 groups of values characterizes the discrepancy between them, since the difference between averages is 16.20 % SiO_2 and the difference between medians is 16.33 % SiO_2. Moreover, the standard deviation of the *low SiO_2* group is slightly smaller than that of the *high SiO_2*, due to the presence of some outliers in the second group.

From figures 6 and 7 one can observe that six sub-populations were isolated in the *low SiO_2* group. Two comprise the higher frequencies: (a) Sub-population 13, from 52.60 to 54.50 %, corresponding to 20.49 % of the data, and (b) Sub-population 14 from 48.95 to 52.60 % corresponding to 47.36 % of the total values (Appendix 3).

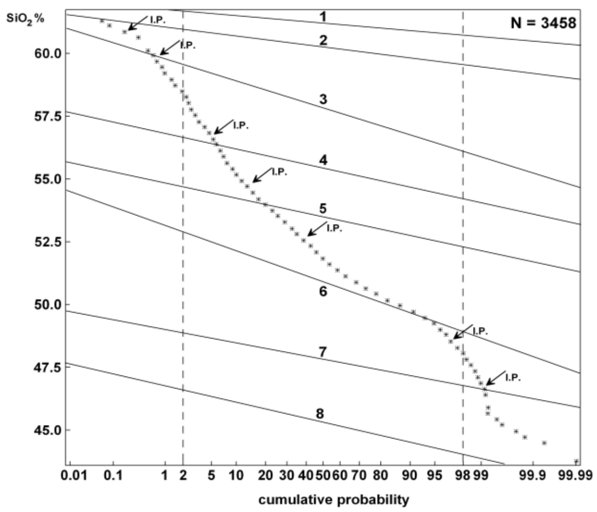


Figure 6. Probability plot for the SiO_2 data set below the *silica gap.*

In the *high SiO_2* group, eight sub-populations were isolated for which sub-population 1 has outliers higher than 75.5 % SiO_2. Sub-populations 3 and 4 together correspond to 13.95 % of the total values: (a) Sub-population 3, ranging from 69.75 to 72.50 % SiO_2, corresponds to 6.20 % of the total data and (b) Sub-population 4, from 66.35 to 69.75 % SiO_2, corresponds to 7.75 % of the data (Appendix 3). These findings, summarized in figure 8, emphasize that the concept of bimodality for the Paraná LIP was induced by the small number of values formerly considered.

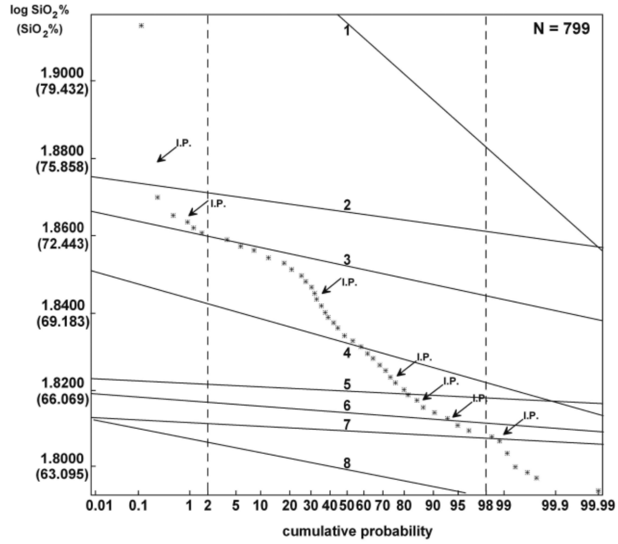


Figure 7. Log-probability plot for the SiO_2 data set above the *silica gap.*

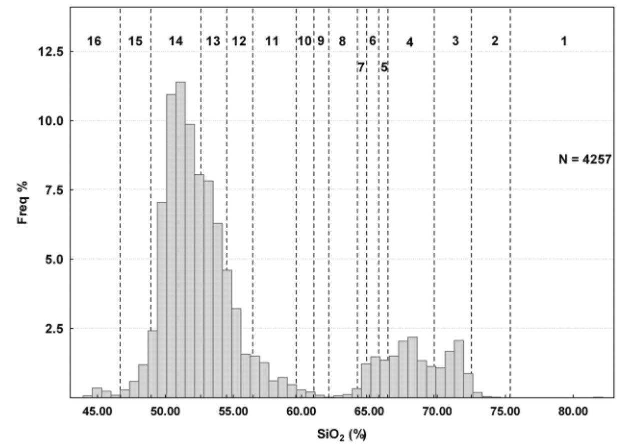


Figure 8. Histogram for SiO_2 showing the sub-populations isolated by probability graph modeling.

3.2. MgO

The values for this oxide range from 0.086 to 22.746 %, and are distributed among 15 sub-populations separated by a gap situated at interval 11 from 2.196 to 2.418 %; its midpoint at 2.307 %, was selected as the cut-off (Fig. 9). The range of greatest concentration of values includes the sub-populations 4 to 6 (3.330 – 6.750 %), where are 69.05 % of the values (Fig. 10, Appendix 3). Sub-populations 12 and 13 (0.394 – 1.650 %) contain 17.33% of the data, setting two modes in the low content group, corresponding to the acidic rocks of the Serra Geral Formation.

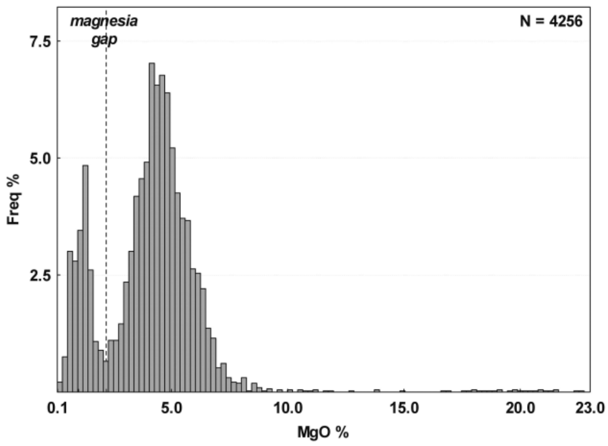


Figure 9. Histogram for MgO showing the *magnesia gap.*

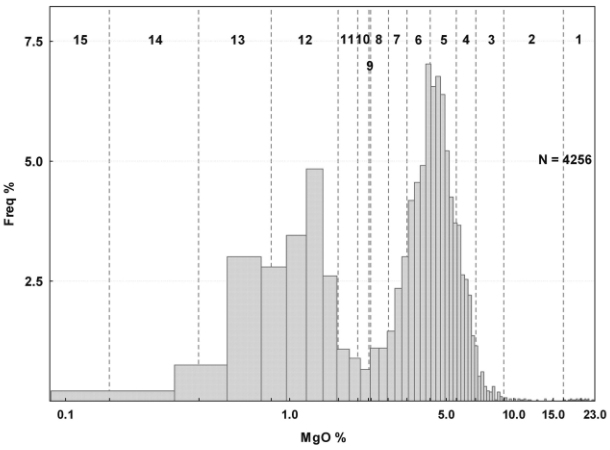


Figure 10. Histogram for MgO showing the sub-populations isolated by probability graph modeling (the y axis is in log-scale).

3.3. TiO_2

Titanium is an important element in characterizing the evolution of igneous rocks because the progression of differentiation is generally characterized by a relative impoverishment in this element. For this reason, Bellieni *et al.* (1984b) established the limit of 2% TiO_2 for the division of the Paraná LIP igneous rocks in LTi (Low Titanium) and HTi (High Titanium). Subsequently, other authors such as Peate *et al.* (1988) established two categories, one for intermediate-basic rocks (comprising three groups) and one for acidic terms (two groups) (Fig. 11). This categorization has been followed by several authors researching the Paraná LIP. In the database investigated in this paper, the values range from 0.252 to 5.647 %, and are distributed among 14 sub-populations with a significant gap at 2.8499 %, the middle point of the class interval from 2.799 to 2.899 % which contains 55 values or 1.29 % of the data (Fig. 4c). Sub-populations from 10 to 12 (0.740 – 2.195%) concentrate 54.36% of the values, while the remaining data are distributed without significant concentrations between the remaining sub-populations (Fig. 12, Appendix 3).

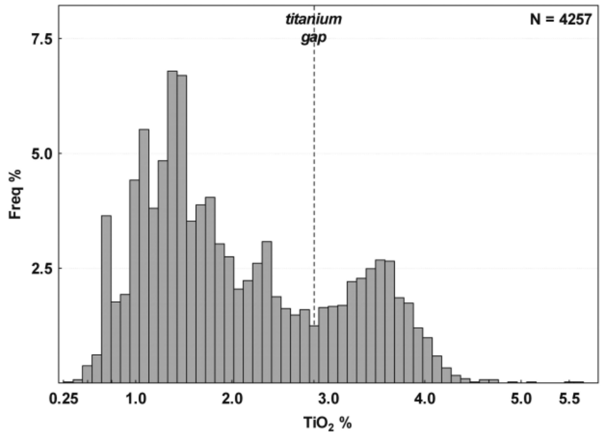


Figure 11. Histogram for TiO_2 showing the *titanium gap.*

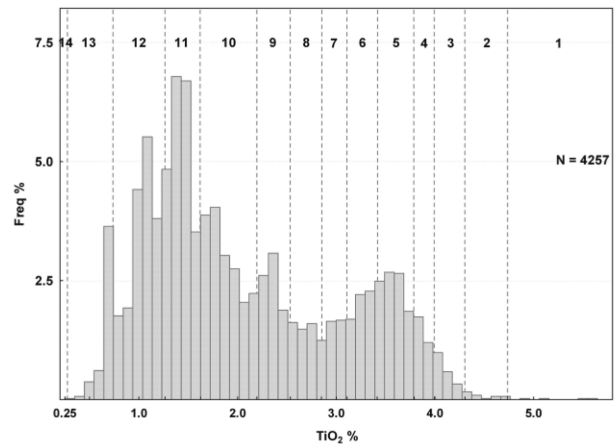


Figure 12. Histogram for TiO_2 showing the sub-populations isolated by probability graph modeling.

3.4. Al_2O_3

This is a major element of which an analysis limited to the histogram can lead to the misinterpretation of a single population with a slightly skewed distribution (Fig. 13). Actually, this data set contains several mixed sub-populations. Thus, Al_2O_3 was taken as an example of geochemical variable without any significant gap. With amplitude from 7.396 to 19.030 %, the values of this oxide are distributed among 14 sub-populations, the sub-set ranging from 12.75 to 14.40 % concentrate 60.29 % of the values .The probability graph of this data sub-set was modeled again aiming at isolating the mixed sub-populations (Figs. 14 and 15). Above and below this group, the statistic frequencies decay regularly to the extremes of the data set (Fig. 16, Appendix 3).

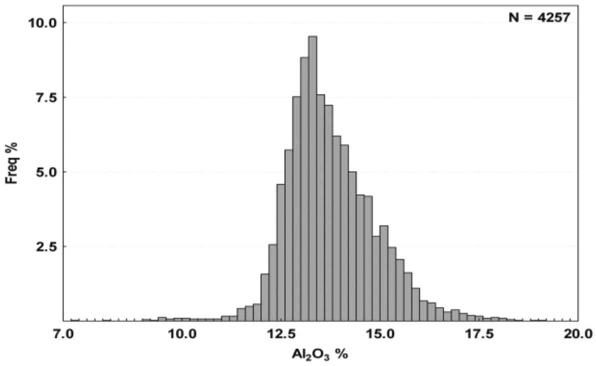


Figure 13. Histogram for Al_2O_3 showing the inexistence of a gap.

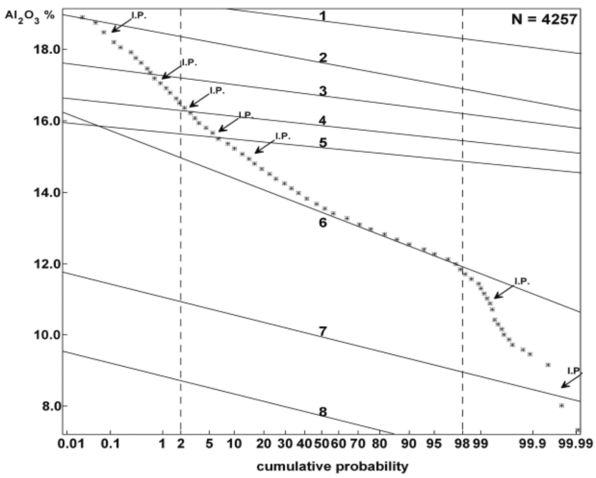


Figure 14. Probability plot for the Al_2O_3 whole data set.

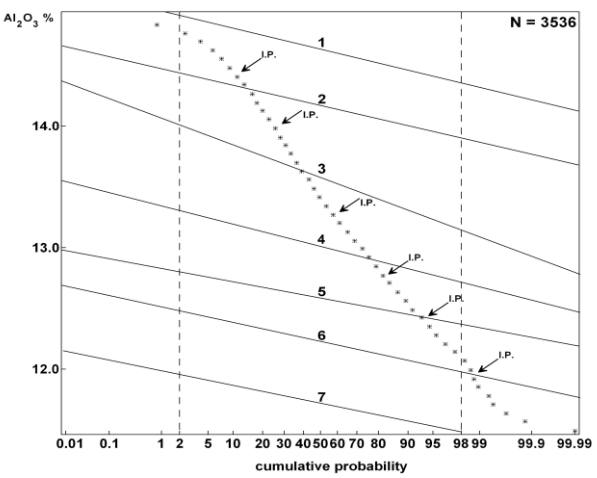


Figure 15. Probability plot for alumina data between 11.5 and 14.9 Al_2O_3%.

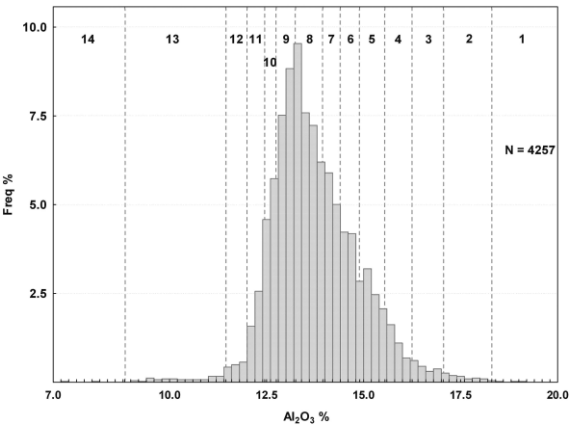


Figure 16. Histogram for Al_2O_3 showing the sub-populations isolated by probability graph modeling.

3.5. FeO_{total}

Ranging from 1.645% to 19.94%, the pattern of the statistical distribution of this oxide could be compared to the SiO_2 and MgO curves, with twelve sub-populations separated by a gap located in class interval 21 between 8.135 to 8.467 %, and a cut-off at 8.301 %, which contains only six values, or 0.169 2% of the total amount of data. The sub-populations 3 to 5 (11.2 - 16.65 %) contain 73.90 % of the values, and sub-populations 9 to 11 (5.05 – 8.01%) contain 17.4 % of the data set (Appendix 3).

3.6. MnO

The probability plot for this oxide comprises fifteen sub-populations. The amplitude varies from 0.00995 % to 2.0 %, with a gap situated in class interval 22 from 0.1229 to 0.1284 % MnO (cut-off selected at 0.12565 %), which corresponds to 33 values or 0.7768 % of the total database. Eight sub-populations fall below the gap, ranging from 0.00995 to 0.1229 %, and seven lie above it, from 0.1284 to 2.0 %. This oxide presents values with amplitude from 0.010 to 2.000 % distributed among 15 sub-populations, of which sub-populations 5 and 6 (0.131-0.263 % MnO) concentrate 83.27 % of the data (Appendix 3).

3.7. CaO

The values for this oxide range from 0.175 to 12.722 %, with four sub-populations isolated in the probability plot and a clear gap in the histogram, located in class interval 16, from 4.2100 to 4.4883 % (cut-off at 4.34915 %), which corresponds to six values, or 0.1409 % of the total. Thus, two sub-populations fall below and two lie above the gap, corresponding to the intervals from 0.175 to 4.01 % CaO, and 4.01 to 12.697 %, respectively. The amplitude of this oxide ranges from 0.175 to 12.697 % distributed among fourteen sub-populations, of which sub-populations from 3 to 6 concentrate 78.74 % of the data. Below the gap, sub-populations 10 to 12 contain 15.32 % of the data set (Appendix 4).

3.8. Na_2O

The distribution of values for this essential component in petrological analyses does not display any statistical gap. Ranging between 1.055 and 8.394%, the values for this oxide are distributed among 13 sub-populations, of which sub-populations 5 to 8 (2.325 to 3.290 % Na_2O) concentrate 78.54 % of the data (Appendix 4).

3.9. K_2O

This oxide presents values between 0.107 to 8.253 %, distributed among 14 sub-populations, of which sub-populations 10 to 13 (0.453 to 2.425 %) concentrate 76.76 % of the values. The six sub-populations revealed in the probability plot between 0.1066 and 8.253 %, are separated by a gap represented by the class interval 23, from 2.8867 to 3.0160 %(cut-off at 2.95135 %), which corresponds to 12 or 0.2818 % of total data (Fig. 17). Seven sub-populations are below the gap, with values from 0.1066 % to 2.8867 %, and seven others are spread above it, with values of 3.0160 % to 8.253 %(Appendix 4).

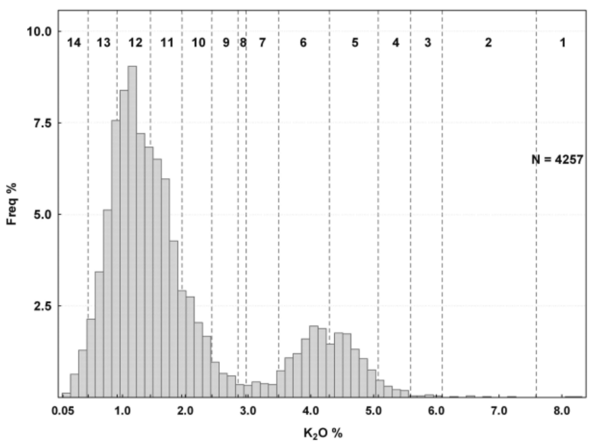


Figure 17. Histogram for K_2O showing the sub-populations isolated by probability graph modeling.

3.10. P_2O_5

With values ranging between 0.02019 and 2.722 %, and fourteen sub-populations, this oxide shows a gap in the class interval 18, from 0.4012 to 0.4243 %, which corresponds to 86 values, or 2.1446 % of the total. Seven sub-populations fall below the gap, with values between 0.02019 and 0.4012 %, and seven sub-populations lie above the gap, with values between 0.4243 and 2.722 %. The values of this oxide scale from 0.020 to 2.722 % P_2O_5, distributed among 14 sub-populations of which, sub-populations 9 to 12, from 0,136 to 0,369 %(cut-off at 0.41275 %), concentrate 61.95 % of the data. Above the gap, sub-populations 5 to 7 contain 27.84 % of the data set (Appendix 4).

3.11. Ba

With values ranging between 5.0 and 3273.4 ppm, this element shows a gap at class interval 33 (848.89 to 875.68 ppm), which contains only 19 values or 0.4898 % of the data set, and the cut-off was selected on its mid-point at 862.285 ppm. The values are distributed among 16 sub-populations. In sub-populations 11 to 14 (231 to 722 ppm) there is a concentration of 77.6 % of the data (Appendix 4).

3.12. Ce

Values for this element range from 4.34 to 275 ppm distributed among 14 sub-populations, of which sub-populations 9 to 12 (26.55 to 120.5 ppm) concentrate 86.97% of the data. The class interval 37, which extends from 141.6 to 145.46 ppm(a cut-off at 143.53 ppm), contains only 0.1808% of the values indicating the cerium gap. Six sub-populations lie above and eight fall below the cerium gap (Fig. 18, Appendix 4).

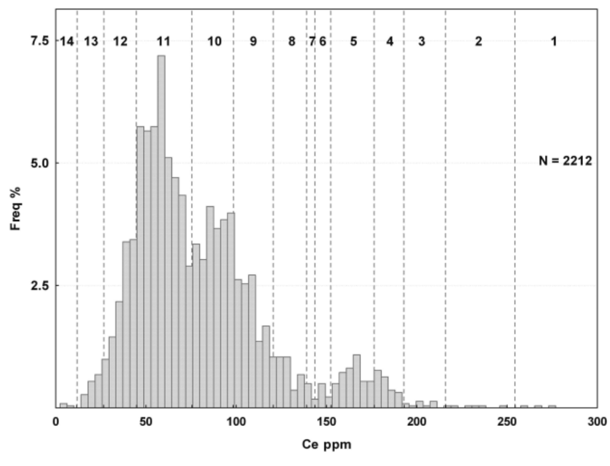


Figure 18. Histogram for Ce showing the sub-populations isolated by probability graph modeling.

3.13. Cr

Values of this element range from 0.500 to 2,000 ppm, distributed among 14 sub-populations without a significant concentration of values, exception made to sub-populations 4 (77.30 – 158.00 ppm) and 12 (6.14 to 23.55 ppm), which contain respectively 23.45 % and 23.91 % of the data (Appendix 5), with no gap. The histogram shows a strong positive asymmetry, so it was necessary to use a logarithmic transformation for the data in the probability graph modeling.

3.14. La

Values for this element range between 2 and 388 ppm, distributed among 15 sub-populations, with 73.03 % of the data concentrated among sub-populations 10 to 13 (16.05-50.95 ppm), and a gap at class interval 31 (68.98 to 71.25 ppm) and a cut-off at 70.115 ppm. Seven sub-populations are situated above and eight below this gap (Appendix 5).

3.15. Ni

Ranging from 1 to 870 ppm, the values of this metal are distributed among 14 sub-populations of which, sub-populations 6 to 9 (22.15 to 90.15 ppm) concentrate 67.79 % of the samples (Appendix 5). There is not any gap characterized in the histogram.

3.16. Rb

This element shows values ranging from 2 to 394 ppm, distributed among 15 sub-populations, of which sub-populations 12 and 13 (15.3 to 60.1 ppm) concentrate 62.65 % of the data (Appendix 5). A gap is noticeable at class interval 21 (117.81 to 123.75 ppm), with only 14 values or 0.363 % of the data set, and a cut-off at 125.88 ppm.

3.17. Sr

Values for this element range from 73.1 to 1125 ppm, distributed among 15 sub-populations, of which sub-populations 10 to 14 (121 to 545.5 ppm Sr) concentrate 84.26 % of the values (Appendix 5), without any significant gap.

3.18. Zr

Values for this element range from 5 to 1278 ppm distributed among 13 sub-populations, with a concentration of 90.54 % of the samples in sub-populations 10 to 12 (73.8 to 360 ppm) and a gap at class interval 40 (515.52 to 528.78 ppm), with only one value or 0.0256 % of the data, and a cut-off at 522.15 ppm. Six sub-populations lie above and seven fall below the gap (Fig. 19, Appendix 5).

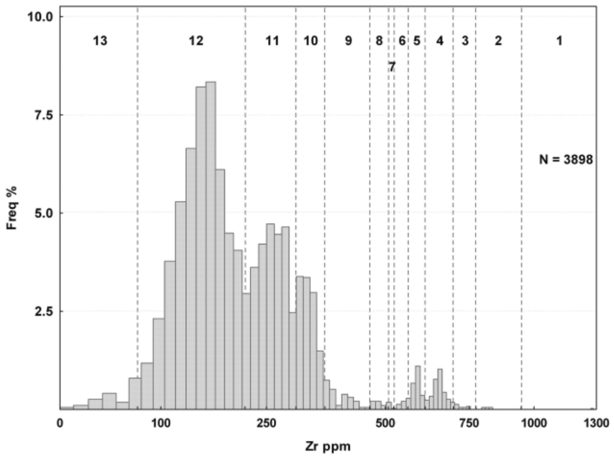


Figure 19. Histogram for Zr showing the sub-populations isolated by probability graph modeling.

3.19. Y

This element shows values that range between 7 ppm and 1001.112, distributed among 13 sub-populations, of which sub-populations 5 to 9 (25.75 to 77.65 ppm) concentrate 89.29 % of the data (Appendix 6), without any detectable gap in the distribution of values.

4. Conclusions

It is necessary to emphasize that the results presented in this article are based on a consistent and robust statistical sample, which summarizes the persevering and meticulous work of dozens of researchers that over the past 40 years have dealt and worked with the Serra Geral Formation in Brazil, Argentina and Paraguay, and the Arapey Group in Uruguay.

All 19 variables - major and minor elements - show from twelve to sixteen sub-populations making up the whole database. The modeling of cumulative frequency curves on probability graphs seems to be a tool able to identify and isolate each sub-population and to characterize it with reliable statistical estimates. It is important to emphasize that as new data will be incorporated to the database, and the statistical sample grows, it is expected that small variations will occur in the values and limits that are presented in this article.

The polymodality of the Paraná LIP geochemical data is systemic, occurring in the data sets of the compatible and incompatible elements, and also with those intrinsic to the primary magmatic activity or those that became enriched by crustal contamination.

Thus, the different sub-populations identified in the data set of each variable suggest: (a) great diversity in processes and perhaps a great number of magma sources, (b) complex evolutionary sequence, (c) heterogeneous crustal contamination. This combination of processes contributed to the great complexity of the Paraná LIP. Because of this highly statistical complexity, the attempts of identifying and characterizing environments and magma types based on complex criteria supported on associations of major and minor elements can provide results that are not satisfactorily applicable to the entire Paraná LIP.

The results of the statistical treatment of virtually every major and minor element indicates the need for a prior stratification of the database taking into account the form of occurrence, intrusive and extrusive, so that the limits of the various populations of SiO_2, MgO and TiO_2, and also other geochemical variables, characterize these specific situations in the rocks of Paraná LIP. It is important to deepen research in order to establish numerical and objective criteria to safely discriminate dykes from sills.

The thresholds obtained from probability plot modeling are non-arbitrary and generic, but real and exclusive to the Paraná LIP. Since these limits were obtained from statistical / numerical modeling, their reliability should be carefully tested before their application to the characterization of units delimited by geological mapping. Nevertheless, they play a role as reference for comparisons between diverse regions and rock types of the Paraná LIP.

Taken into account the relatively small number of sub-surface geochemical samples and their restriction to a single NS section, the authors believe that the previous regional models, which were established for both surface and deep portions of the Paraná LIP seem to be questionable. For the construction of reliable magma type models it is necessary to increase sampling density so as to have the Paraná LIP covered evenly.

In order to facilitate the task of integrating data emerging from coming researches, the authors suggest that geochemical data tables be published as follows:

(I) analytical results should be published as received from the laboratory, but if the author prefers to present the recalculation to an anhydrous base, it is mandatory (a) to include a column with LOI and (b) the recalculation of the values should be mentioned at the bottom of the data table;

(ii) iron content should be published as received from laboratory (FeO_{total}). Publication of recalculated contents of FeO and Fe_2O_3 must be avoided since the proportions between the two forms of iron are arbitrary, depending on the rock type and change the original values. But if that is preferred, the ratio used to recalculate the iron for each rock type must be mentioned at the bottom of the data table;

(iii) the adoption of geographic coordinates is advisable even for restricted areas, as the Paraná LIP extends over one million sq km and is hundreds of meters thick;

(iv) if the samples are referred in projected UTM coordinates, the central meridian and the projection system must be informed;

(v) even in road sections of small extent, each sample must have its coordinate triplet (easting, northing, altitude) recorded as accurately as possible, thus avoiding the assignment of the same coordinates at all points that compose the section, and,

(vi) the vertical datum adopted for the altitude must be cited at the bottom of the respective data table.

These suggestions are intended to facilitate the aggregation of the new data to the database compiled and standardized for this research serving as a homogenous knowledge base of the Paraná LIP.

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References

Bellieni, G., Brotzu, P., Comin-Chiaramonti, P., Ernesto, M., Melfi, A.J., Pacca, I.G., Piccirillo, E.M. & Stolfa, D. 1983. Petrological and paleomagnetic data on the plateau basalt to rhyolite sequences of the southern Paraná Basin (Brazil). *Anais da Academia Brasileira de Ciências*, 55: 355-383.

Bellieni, G., Brotzu, P., Comin-Chiaramonti, P., Ernesto, M., Melfi, A.J., Pacca, I.G. & Piccirillo, E. M. 1984a. Flood basalt to rhyolite suites in the southern Paraná plateau (Brazil): paleomagnetism, petrogenesis and geodynamic implications. *Journal of Petrology*, 25: 579-618.

Bellieni, G., Comin-Chiaramonti, P., Marques, L.S., Melfi, A.J., Picirillo, E.M. & Stolfa, D. 1984b. Low-pressure evolution of basaltic sills from boreholes in the Paraná Basin, Brazil. *Tschermaks Mineralogische und Petrographische Mitteilungen*, 33: 25-47.

Bellieni, G., Comin-Chiaramonti, P., Marques, L.S., Melfi, A.J., Papatrechas, C., Piccirillo, E.M., Nardy, A.J.R., Roisenberg, A. & Stolfa, D. 1986. Petrogenetic aspects of acid and basaltic lavas from the Paraná plateau (Brazil): mineralogical and petrochemical aspects, *Journal of Petrology*, 27: 915- 944

Bentzen, A. & Sinclair, A.J. 2002. *P-RES Version 2.0. A Computer Program To Aid In The Interpretation Of Polymetallic Assay, Geochemical, Environmental and Quality Control Data.* University of British Columbia. Available :<http://eos.ubc.ca/research/mininv/files.html> Acessado 12 de Junho de 2010.

Bossi, J. & Navarro, R. 1988. Magmatismo mesozoico. *In*: *Geología del Uruguay.* Montevideo, Universidad de la Republica, v. 2, p. 698-757.

Bossi, J. & Schilipov, A. 2007. *Rocas igneas básicas del Uruguay*. Montevideo, Universidad de la Republica, Facultad de Agronomia., 364p.

Bryan, S.E., Riley, T.R., Jerram, D.A., Leat, P.T. & Stephens, C.J. 2002. *Silicic volcanism: an under-valued componentes of large igneous provinces and volcanic rifted margins. In*: Menzies, M.A., Klemperer, S.L., Ebinger, C.J. & Baker, J. (Ed.) Magmatic Rifted Margins: Geological Society of America, Special Paper 362: 99-120.

Campanha, G.A.C. 1991. *Tectônica proterozóica no alto e médio vale do Ribeira, estados de São Paulo e Paraná*. São Paulo. 296p. Tese de Doutorado. Instituto de Geociências, Universidade de São Paulo.

Chies, J.O. 1991. P*etrologia e geoquímica do vulcanismo mesozóico da Bacia do Paraná na região ocidental do Rio Grande do Sul e Santa Catarina.* Porto Alegre, 223 p. Dissertação de Mestrado. Instituto de Geociências, Universidade Federal do Rio Grande do Sul.

Fodor, R. V., Corwin, C. & Roisenberg, A. 1985. Petrology of Serra Geral (Paraná) continental flood basalts, southern Brazil: crustal contamination, source material and south Atlantic magmatism. *Contributions to Mineralogy and Petrology,* 91: 54-65.

Garland, F., Hawkesworth, C.J. & Mantovani, M.S.M. 1995. Description and petrogenesis of the Paraná rhyolites, southern Brazil. *Journal of Petrology,* 36: 1193-1227.

GPSvisualizer. 2010. Disponível em: <http://www.gpsvisualizer.com/>. Acessado em Setembro a Novembro 2010.

Hildreth W. & Moorbath S. 1988. Crustal contributions to arc magmatism in the Andes of Central Chile. *Contributions to Mineralogy and Petrology*, 98: 455-489.

JICA. Japan International Cooperation Agency. 2005. *Geochemical analysis from igneous rocks of the Paraná Basin*. Brasilia. Internal Report.

Kirstein, L.A., Peate, D.W., Hawkesworth, C.J., Turner, S.P., Harris, C.H. & Mantovani, M.S.M. 2000. Early cretaceous basaltic and rhyolitic magmatism in southern Uruguay associated with the opening of the south Atlantic. *Journal of Petrology,* 41: 1413-1438.

Licht, O.A.B. & Arioli, E.E. 1998. *Prospecção mineral no Terceiro Planalto do Paraná.* Curitiba, Minerais do Paraná. (Relatório Interno). 193p.

Lopes, K. 2008. *Caracterização morfológica, petrográfica e química dos derrames da província magmática do Paraná com ênfase para as rochas aflorantes no município de Guarapuava- PR.* Curitiba, 191p. Dissertação de Mestrado, Departamento de Geologia, Universidade Federal do Paraná.

Machado, F.B. 2005. *Geologia e aspectos petrológicos das rochas intrusivas e extrusivas de parte da borda leste da Bacia do Paraná no estado de São Paulo*. Rio Claro, 194p. Dissertação de Mestrado, Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista Júlio de Mesquita Filho.

Machado, F.B. 2009. *Petrologia e caracterização geoquímica das fontes mantélicas dos derrames de lava da região noroeste da província magmática do Paraná*. Rio Claro, 260p. Tese de Doutoramento, Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista Júlio de Mesquita Filho.

Macedo, A.B. & Rüegg, N.R. 1974. Aplicação da análise fatorial ao estudo de elementos principais nas rochas basálticas da Bacia do Paraná. *In:* CONGRESSO BRASILEIRO DE GEOLOGIA, 28., 1974. *Anais...* Porto Alegre, SBG, v.7, p. 49-56.

Maniesi, V. & Oliveira, M.A.F. 1997. Petrologia das soleiras de diabásio de Reserva e Salto do Itararé, PR. *Geochimica Brasiliensis,* 11: 153-169.

Mantovani, M.S.M., Marques, L.S., de Sousa, M.A., Civetta, L., Atalla, L. & Innocenti, F. 1985. Trace elements and strontium isotope constraints on the origin and evolution of Paraná continental flood basalts of Santa Catarina state (southern Brazil). *Journal of Petrology,* 26: 187-209.

Marimon, M.P.C., Moreira, M.L.O. & Ayala, L. 1983. Formação Serra Geral no sul do Brasil: novos dados de razões isotópicas Sr^{87}/Sr^{86} e implicações com a gênese das rochas desta Formação. *In*: SIMPÓSIO SUL-BRASILEIRO DE GEOLOGIA, 1, 1974, Porto Alegre. *Proceedings...* Porto Alegre, SBG, p. 69-81.

Mincato, R.L. 2000. *Metalogenia dos elementos do grupo da platina com base na estratigrafia e geoquímica da província ígnea continental do Paraná*. Campinas, 172 p. Tese de Doutorado, Universidade Estadual de Campinas.

Nardy, A. J. R. 1996. *Geologia e petrologia do vulcanismo mesozóico da região central da Bacia do Paraná.* Rio Claro, 316p. Tese de Doutorado, Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista Júlio de Mesquita Filho.

Nardy, A.J.R., Machado, F.B. & Oliveira, M.A.F. 2008. As rochas vulcânicas mesozóicas ácidas da Bacia do Paraná: litoestratigrafia e considerações geoquímico-estratigráficas. *Revista Brasileira de Geociências*, 38: 178-195.

Peate, D.W. 1989. *Stratigraphy and petrogenesis of the Paraná continental flood basalts, southern Brazil*. London, 360 p. Tese de Doutorado, Department of Earth Sciences, The Open University.

Peate, D.W. & Hawkesworth, C.J. 1996. Lithospheric to astenospheric transition in low-ti flood basalts from southern Paraná, Brazil. *Chemical Geology,* 127: 1-24.

Peate, D.W., Mantovani, M.S.M. & Hawkesworth, C.J. 1988. Geochemical stratigraphy of the Paraná continental flood basalt: borehole evidence. *Revista Brasileira de Geociências,* 18: 212-221.

Peate D.W., Hawkesworth C.J. & Mantovani M.S.M. 1992. Chemical stratigraphy of the Paraná lavas (South America): classification of magma types and their spatial distribution. *Bulletin of Volcanology*, 55:119-139.

Peate, D.W., Hawkesworth, C.J., Mantovani, M.S.M., Rogers, N.W. & Turner, S.P. 1999. Petrogenesis and stratigraphy of the high-ti/y Urubici magma type in the Paraná flood basalt province and implications for the nature of 'Dupal'-type mantle in the south Atlantic region. *Journal of Petrology,* 40: 451-473.

Petersohn, E. 2006. *Evolução térmica de soleiras encaixadas nas formações Irati e Ponta Grossa (Bacia do Paraná) no estado do Paraná – contribuição para o entendimento da evolução dos sistemas petrolíferos Irati – Rio Bonito/Pirambóia e Ponta Grossa – Itararé*. Curitiba, 157p. Dissertação de Mestrado, Curso de Pós Graduação em Geologia, Setor de Ciências da Terra, Universidade Federal do Paraná.

Petrini, R., Civetta, L., Piccirillo, E. M., Bellieni, G., Comin-Chiaramonti, P., Marques, L. S. & Melfi, A. J. 1987. Mantle heterogeneity and crustal contamination in the genesis of low-Ti continental flood basalts from the Paraná plateau (Brazil): Sr-Nd isotopes and geochemical evidence. *Journal of Petrology,* 28: 701-726.

Piccirillo, E.M. & Melfi, A.J. (Ed). 1988. The mesozoic flood volcanism of the Paraná Basin. São Paulo, IAG-USP, 600 p.

Piccirillo, E.M., Comin-Chiaramonti, P., Melfi, A. J., Stolfa, D., Bellieni, G., Marques, L.S., Giaretta, A., Nardy, A.J.R., Pinese, J.P.P., Raposo, M.I.B. & Roisenberg, A. 1988a. *Petrochemistry of continental flood basalt-rhyolite suites and related intrusives from the Paraná Basin (Brazil). In*: PICCIRILLO, E. M. & MELFI, A. J. (Ed). The mesozoic flood volcanism of the Paraná Basin. IAG-USP. São Paulo, IAG-USP, p. 107-156.

Piccirillo, E.M., Melfi, A.J. & Nardy, A.J.R. 1988b. *Geological and magmatic aspects of the Paraná Basin – an introduction. In:* Piccirillo, E. M.& Melfi, A. J. (Ed). 1988. The mesozoic flood volcanism of the Paraná Basin. IAG-USP. São Paulo, IAG-USP, p. 1-13.

Piccirillo, E.M., Civetta, L., Petrini, R., Longinelli, G., Bellieni, G., Comin-Chiaramonti, P., Marques, L.S. & Melfi, A.J. 1989a. Regional variations within the Paraná flood basalts (southern Brazil): evidence for subcontinental mantle heterogeneity and crustal contamination. *Chemical Geology,* 75: 103-122.

Piccirillo, E.M., Raposo, M.I.B., Melfi, A.J., Comin-Chiaramonti, P., Bellieni, G., Cordani, U.G. & Kawashita, K. 1989b. Bimodal fissural volcanic suites from the Paraná Basin (Brazil): K-Ar age, Sr-isotopes and geochemistry. *Geochimica Brasiliensis*, 1: 53-69.

Regelous, M. 1993. *Geochemistry of dolerites from the Paraná flood basalt province, southern Brazil*. London, 200p. Tese de Doutorado, The Open University, Milton Keynes.

Renne, P.R., Deckart, K., Ernesto, M., Féraud, G. & Piccirillo, E.M. 1996. Age of the Ponta Grossa dike swarm (Brazil): and implications to Paraná flood volcanism. *Earth Planetary Science Letters,* 144: 199-211.

Roisenberg, A. 1989. *Petrologia e geoquímica do vulcanismo ácido mesozóico da província meridional da Bacia do Paraná*. Porto Alegre, 285p. Tese de Doutorado, Instituto de Geociências, Universidade Federal do Rio Grande do Sul.

Romanini, S.J. & Albuquerque, L.F. 2000. *Aspectos geológicos, geoquímicos e potencialidade em depósitos de Ni-Cu-EGP do magmatismo da Bacia do Paraná. Projeto Platina e associados*. Porto Alegre, Companhia de Pesquisa de Recursos Minerais. 2. ed.

Rüegg, N. 1975. *Modelos de variação química na província basáltica do Brasil meridional. Características de teor, distribuição geográfica e diferenciação*. São Paulo, 302p. 2v. Tese de Livre Docência, Instituto de Geociências, Universidade de São Paulo.

Sinclair, A.J. 1974. Selection of threshold values in geochemical data using probability graphs. *Journal of Geochemical Exploration*. 3: 129-149.

Sinclair, A.J. 1976. Applications of probability graphs in mineral exploration. *The Association of Exploration Geochemistry. Spec. Vol 4.*

Sinclair, A.J. & Blackwell, G.H. 2006. *Applied mineral* *inventory estimation*. Cambridge. Cambridge University Press. 381p

Statsoft, Inc. 2008. *Statistica (data analysis software system)*, v. 8.0. Disponível em: <http.www.statsoft-.com> Accessado em 15 de Jun. de 2010.

Thiede, D.S. & Vasconcelos, P.M. 2008. Paraná flood basalts: rapid extrusion hypothesis supported by new $^{40}Ar/^{39}Ar$ results. *In:* CONGRESSO BRASILEIRO DE GEOLOGIA, 44, Curitiba. *Proceedings*... Curitiba, SBG, 2008.

Thiede, D.S. & Vasconcelos, P.M. 2010. Paraná flood basalts: Rapid extrusion hypothesis confirmed by new $^{40}Ar/^{39}Ar$ results. *Geology,* 38(8): 747-750.

Torres, M., Oliveira, M.A.F., Nardy, A.C.R. & Machado, F.B. 2008. Litogeoquímica e quimioestratigrafia da província magmática do Paraná, no município de Araçatuba (SP). *Revista Brasileira de Geociências,* 38: 544-553.

Turner, S.P., Peate, D.W., Hawkesworth, C.J. & Mantovani, M.S.M. 1999. Chemical stratigraphy od the Paraná basalt succession in western Uruguay: further evidence for the diachronous nature of the Paraná magma types. *Journal of Geodynamics,* 28: 459-469.

Turner, S.P., Hawkesworth, C.J., Gallagher, K., Stewart, K., Peate, D. & Mantovani, M.S.M. 1996. Mantle plumes, flood basalts, and thermal models for melt generation beneath continents: assessment of a conductive heating model and application to the Paraná. *Journal of Geophysical Research*, 101:11503-11518

Vanzella., G.A., Vasconcellos, E.M.G., Mesquita, M.J.M.& Pinese, J.P.P. 2004. Caracterização petrográfica e geoquímica de diques mesozóicos à noroeste de Rio Branco do Sul, PR. *Geochimica Brasiliensis*, 18(2): 064-076.

Viero, A.P. 1992. *Petrologia e geoquímica do complexo básico de Lomba Grande, RS*. Porto Alegre, 176p. Dissertação de Mestrado, Instituto de Geociências, Universidade Federal do Rio Grande do Sul.

Whittingham, A. 1991. *Stratigraphy and petrogenesis of the volcanic formations associated with the opening of the south Atlantic, southern Brazil*. Tese de Doutorado, University of Oxford.

Wildner, W., Licht, O.A.B. & Arioli, E.E. 2006. *Mapeamento do SW do estado do Paraná*. Curitiba, MINEROPAR – CPRM. 94p.

Appendix 1. *Step-by-step* procedures adopted for the constitution, standardization, review and consistency check of the lithogeochemical database for the Paraná LIP:

Geochemical data

1. Selection of books, thesis, dissertations, monographs, articles, and databases published, provided by researchers or available on the Internet with lithogeochemical data from different research projects on the Paraná LIP,
2. Design of a spreadsheet whose structure is adjusted as the work progresses,
3. Oxide content data entry and check for immediate correction of transcription or digitization errors by using an extra column with the sum of the oxide values typed in for comparison to published data,
4. Suppression of defective samples, either for lacking content of oxides or other elements essential to the analysis, or for being of historical interest only as reliable analytical methods were unavailable until the 1960s,
5. Querying of the data sources for other relevant data such as rock type, coordinates, location, sample type and form of occurrence,
6. Identification of samples with oxide content published on a hydrated (as received from laboratory) or on an anhydrous basis (recalculated to 100%, disregarding the loss on ignition) – only Peate & Hawkesworth (1996), Piccirillo & Melfi (1988) and Piccirillo *et al.* (1989b) specify at the bottom of the data tables that the values were recalculated and published on an anhydrous basis, the sums of oxides in Romanini & Albuquerque (2000) were considered as published on a hydrated basis because their values were very different from 100%, despite stated to have been recalculated on an anhydrous basis,
7. Creation of two new blocks of columns to store standardized oxide contents as hydrated, anhydrous, and recalculated to 100%,
8. Sorting of the database by using a combination of three elements SiO_2, Al_2O_3 and TiO_2 for make it easy to identify samples that were repeated in two or more sources even with different identification code,
9. Visual observation and selection of pairs or triplets of identical samples (same contents of oxides and minor elements),
10. Consolidation of the data and information considering only one of the duplicate or triplicate samples,
11. Suppression of unnecessary duplicate or triplicate samples,
12. Identification of extrusive and intrusive rocks samples, as indicated by the authors. For samples collected in drill holes, a comparison was made with the geological profile of the well to the portrayal of the type of occurrence. In the absence of other indications, the sample was arbitrarily considered as extrusive,
13. When the total content of FeO_{total} was stated along those of Fe_2O_3 and FeO, the first one was prioritized for being the value reported by the laboratory. Nevertheless, the three forms of iron content were kept in the database for future calculations. That is really a problem because in many data sources the FeO and Fe_2O_3 values were recalculated from FeO_{total} values by using unpublished correction factors specific for each rock type, which makes it is impossible to know the original values,

Data positioning

14. When coordinates were not included in the published data source, the location maps were digitized, and georeferenced. The original points of the georeferenced maps had their geographic or UTM coordinates recorded in an ArcView environment,
15. All UTM projected coordinates were converted to geographic decimal degrees with five decimal places using WGS84 as the reference system,
16. For samples with either unexpressed coordinates or no location on map, but with a description of their collection sites, outcrop or well, the geographic coordinates in decimal degrees were obtained with the Google Earth application (2010),
17. Altitudes of outcrop samples were standardized in a SRTM digital elevation model through the GPSVisualizer website (GPSvisualizer, 2010), from coordinates in WGS84 geographic decimal degrees,
18. Samples collected from wells had their published altitudes maintained since the discrepancies between published and SRTM-DEM altitudes were irrelevant,
19. When the altitude of the sample was not published, but its code name is linked to the depth from the well collar, the altitude of the sample was calculated from the altitude of the well collar obtained directly on the website of the National Petroleum Agency, Database Exploration and Production - BDEP,
20. Geographic decimal degrees latitude and longitude were also converted into projected coordinates (Polyconic Brazil system – SAD69 Datum),
21. Compilation of the final database with 4,257 geochemical samples.

Appendix 2. Statistical estimates for major and minor elements in the Paraná LIP.

Oxide / element	N	Minimum	1st quartile (25%)	Median	Average	3rd quartile (75%)	Maximum	Standard deviation	Number of class intervals
SiO_2 (%)	4257	43.95	50.86	52.60	55.26	55.75	82.18	6.76	56
MgO (%)	4256	0.086	3.057	4.27	4.09	5.15	22.75	2.19	55
TiO_2 (%)	4257	0.25	1.29	1.77	2.06	2.87	5.65	0.98	102
Al_2O_3 (%)	4257	7.39	13.02	13.59	13.76	14.41	19.03	1.14	56
FeO_{total} (%)	3545	1.64	11.06	12.97	12.19	14.53	19.95	3.29	362
MnO (%)	4248	0.009	0.16	0.19	0.18	0.21	2.00	0.05	103
CaO (%)	4257	0.17	6.84	8.39	7.60	9.44	12.69	2.72	46
Na_2O (%)	4257	1.06	2.51	2.74	2.79	3.03	8.39	0.47	154
K_2O (%)	4257	0.11	1.04	1.45	1.91	2.19	8.25	1.28	64
P_2O_5 (%)	4010	0.02	0.22	0.30	0.37	0.47	2.72	0.23	118
Ba (ppm)	3879	5.00	330.00	453.00	511.85	640.00	3273.40	265.26	123
Ce (ppm)	2212	4.34	53.00	71.00	80.04	98.00	275.00	38.00	71
Cr (ppm)	3687	0.50	20.00	45.00	77.48	96.00	2000.00	116.30	172
La (ppm)	2316	2.00	22.00	31.00	36.91	46.20	388.00	22.54	171
Ni (ppm)	3846	1.00	16.00	37.00	42.99	56.00	870.00	52.40	166
Rb (ppm)	3856	2.00	26.00	39.73	64.56	81.00	394.00	58.44	67
Sr (ppm)	3988	2.00	186.00	268.50	310.64	406.00	1125.00	174.95	64
Zr (ppm)	3898	5.00	151.00	203.00	237.61	283.00	1278.00	131.07	329
Y (ppm)	3750	7.00	31.00	37.00	41.88	45.00	1001.11	30.23	97

Observation: the number of class intervals was used to draw histograms and probability plots.

Appendix 3. Summary of SiO_2, MgO, TiO_2, Al_2O_3, FeO_{total} and MnO sub-populations and its statistical estimates, isolated by probability graphs modeling. The underscored values indicate that the probability graph, or part of it, was modeled with log transformed values.

SiO_2 %

Sub-pop	%	N	from	to	mean	sd
1	0.05	2	75.350	82.175	82.100	0.0154
2	0.12	5	72.500	75.350	73.400	0.0024
3	6.20	264	69.750	72.500	71.200	0.0037
4	7.75	330	66.350	69.750	68.000	0.0049
5	2.02	86	65.700	66.350	66.000	0.0009
6	1.48	63	64.800	65.700	65.200	0.0013
7	0.94	40	64.150	64.800	64.500	0.0008
8	0.21	9	62.020	64.150	63.000	0.0035
9	0.15	6	60.900	62.020	61.200	0.2330
10	0.45	19	59.600	60.900	60.300	0.3430
11	3.48	148	56.450	59.600	57.900	0.8460
12	7.03	299	54.500	56.450	55.500	0.5900
13	20.49	872	52.600	54.500	53.500	0.5800
14	47.36	2016	48.950	52.600	50.900	0.9680
15	1.54	65	46.700	48.950	47.800	0.5100
16	0.75	32	43.951	46.700	45.300	0.6230

MgO %

Sub-pop	%	N	from	to	mean	sd
1	0.61	26	16.650	22.746	19.800	0.0340
2	0.34	15	9.050	16.650	12.100	0.0663
3	2.28	97	6.750	9.050	7.780	0.0366
4	13.32	567	5.545	6.750	6.140	0.0264
5	35.58	1514	4.230	5.545	4.810	0.0351
6	20.15	858	3.330	4.230	3.790	0.0308
7	5.41	230	2.725	3.330	3.030	0.0233
8	1.92	82	2.307	2.725	2.510	0.0183
9	0.22	10	2.245	2.307	2.290	0.0192
10	0.76	32	2.015	2.245	2.120	0.0621
11	1.31	56	1.650	2.015	1.840	0.1010
12	13.25	564	0.828	1.650	1.230	0.2160
13	4.08	174	0.394	0.828	0.666	0.0933
14	0.56	24	0.157	0.394	0.390	0.0382
15	0.21	9	0.086	0.157	0.179	0.0643

TiO_2 %

Sub-pop	%	N	from	to	mean	sd
1	0.10	4	4.735	5.647	5.26	0.0274
2	0.28	12	4.305	4.735	4.55	0.0129
3	1.63	69	3.995	4.305	4.14	0.00938
4	3.02	129	3.790	3.995	3.90	0.00741
5	9.61	409	3.415	3.790	3.59	0.0134
6	6.51	277	3.110	3.415	3.27	0.0118
7	4.14	176	2.850	3.110	2.98	0.0103
8	4.58	195	2.535	2.850	2.69	0.0846
9	8.27	352	2.195	2.535	3.36	0.0924
10	16.21	690	1.625	2.195	1.90	0.1540
11	21.68	923	1.265	1.625	1.45	0.1040
12	16.47	701	0.740	1.265	1.09	0.0996
13	7.37	314	0.273	0.740	0.729	0.0917
14	0.15	6	0.252	0.273	0.412	0.0876

Al_2O_3 %

Sub-pop	%	N	from	to	mean	sd
1	0.09	4	18.300	19.030	18.800	0.2370
2	0.76	32	17.050	18.300	17.600	0.3500
3	1.50	64	16.250	17.050	16.700	0.2390
4	3.87	165	15.550	16.250	15.900	0.2050
5	8.78	374	14.900	15.550	15.200	0.1830
6	9.50	404	14.400	14.990	14.600	0.1350
7	12.75	543	13.950	14.400	14.200	0.1310
8	27.64	1177	13.250	13.950	13.600	0.2100
9	19.90	847	12.750	13.250	13.000	0.1420
10	8.99	383	12.450	12.750	12.600	0.1050
11	4.50	192	12.000	12.450	12.200	0.1220
12	1.01	43	11.450	12.000	11.700	0.1170
13	0.68	29	8.845	11.450	9.960	0.4810
14	0.03	1	7.396	8.845	7.730	0.4830

FeO total %

Sub-pop	%	N	from	to	mean	sd
1	0.12	4	19.1	19.949	19.7	0.312
2	1.45	51	16.650	19.100	17.8	0.633
3	11.55	410	15.300	16.650	15.9	0.407
4	34.45	1221	13.150	15.300	14.2	0.645
5	27.90	989	11.200	13.150	12.2	0.581
6	6.57	233	9.260	11.200	10.3	0.494
7	0.14	5	8.325	9.260	8.77	0.228
8	0.11	4	8.010	8.325	8.16	0.0888
9	2.32	82	7.165	8.010	7.59	0.225
10	8.00	284	5.830	7.165	6.47	0.362
11	6.98	247	5.050	5.830	5.27	0.323
12	0.41	15	1.646	5.050	4.1	0.691

MnO %

Sub-pop	%	N	from	to	mean	sd
1	0.04	2	1.022	2.000	1.970	0.0709
2	0.09	4	0.395	1.022	0.513	0.0421
3	0.27	12	0.304	0.395	0.332	0.0214
4	0.37	16	0.263	0.304	0.289	0.0121
5	77.82	3306	0.152	0.263	0.197	0.0538
6	5.45	231	0.131	0.152	0.140	0.0157
7	0.65	28	0.126	0.131	0.129	0.0523
8	2.20	94	0.119	0.126	0.122	0.0015
9	3.94	168	0.105	0.119	0.112	0.0035
10	2.41	103	0.096	0.105	0.101	0.0022
11	2.36	100	0.085	0.096	0.091	0.0026
12	1.62	69	0.075	0.085	0.080	0.0026
13	0.84	35	0.068	0.075	0.071	0.0018
14	1.73	73	0.040	0.068	0.053	0.0076
15	0.20	8	0.010	0.040	0.028	0.0070

Appendix 4. Summary of CaO, Na_2O, K_2O, P_2O_5, Ba and Ce sub-populations and its statistical estimates, isolated by probability graph modeling. The underscored values indicate that the probability graph, or part of it, was modeled with log transformed values.

CaO %

Sub-pop	%	N	from	to	mean	sd
1	0.11	4	12.350	12.697	12.6	0.1260
2	0.58	25	11.400	12.350	11.8	0.2430
3	8.73	372	10.300	11.400	10.8	0.3190
4	33.32	1418	8.650	10.300	9.43	0.4740
5	27.92	1189	7.505	8.650	8.11	0.3540
6	8.77	373	5.980	7.505	6.76	0.4240
7	1.74	74	4.315	5.980	5.2	0.4220
8	0.62	26	3.760	4.315	4.01	0.1270
9	1.28	54	3.395	3.760	3.56	0.0989
10	9.62	410	2.495	3.395	2.96	0.2370
11	3.23	137	1.905	2.495	2.17	0.1650
12	2.47	105	1.515	1.905	1.72	0.1240
13	1.23	52	1.030	1.515	1.29	0.1360
14	0.40	17	0.175	1.030	0.635	0.2030

Na_2O %

Sub-pop	%	N	from	to	mean	sd
1	0.09	3	6.070	8.394	8.37	0.0715
2	0.77	29	3.500	6.070	4.88	0.0488
3	5.24	196	3.460	3.500	3.71	0.0163
4	5.38	201	3.290	3.460	3.38	0.00642
5	12.21	458	3.025	3.290	3.15	0.0103
6	19.41	727	2.800	3.025	2.91	0.0102
7	32.11	1203	2.520	2.800	2.66	0.0136
8	14.81	555	2.325	2.520	2.42	0.0105
9	6.74	252	2.095	2.325	2.22	0.0119
10	1.65	62	1.855	2.095	1.94	0.0118
11	0.77	29	1.715	1.855	1.79	0.0104
12	0.54	20	1.595	1.715	1.63	0.0113
13	0.29	11	1.055	1.595	1.36	0.0398

K_2O %

Sub-pop	%	N	from	to	mean	sd
1	0.05	2	7.590	8.253	8.14	0.00855
2	0.12	5	6.095	7.590	6.66	0.02120
3	0.18	8	5.590	6.095	5.87	0.01020
4	0.84	36	5.075	5.590	5.32	0.01050
5	8.16	347	4.295	5.075	4.62	0.02070
6	8.77	373	3.485	4.295	3.92	0.02450
7	1.36	58	2.965	3.485	3.19	0.01800
8	0.27	12	2.840	2.965	2.91	0.0420
9	1.91	81	2.425	2.840	2.63	0.1130
10	7.42	316	1.945	2.425	2.18	0.1330
11	20.19	859	1.445	1.945	1.69	0.1420
12	34.38	1463	0.917	1.445	1.17	0.1590
13	14.77	629	0.453	0.917	0.712	0.1340
14	1.59	68	0.107	0.453	0.306	0.0778

P_2O_5 %

Sub-pop	%	N	from	to	mean	sd
1	0.25	10	2.375	2.722	2.56	0.0161
2	0.44	18	1.180	2.375	1.67	0.0770
3	0.82	33	0.926	1.180	1.04	0.0285
4	2.77	111	0.737	0.926	0.822	0.0285
5	5.85	235	0.620	0.737	0.678	0.0225
6	8.26	331	0.524	0.620	0.569	0.0215
7	13.73	551	0.415	0.524	0.468	0.0276
8	4.30	172	0.369	0.415	0.392	0.0124
9	8.56	343	0.318	0.369	0.341	0.0150
10	16.16	648	0.257	0.318	0.289	0.0181
11	28.30	1135	0.183	0.257	0.218	0.0215
12	8.93	358	0.136	0.183	0.161	0.0142
13	1.43	57	0.093	0.136	0.115	0.0116
14	0.21	8	0.020	0.093	0.05	0.0226

Ba ppm

Sub-pop	%	N	from	to	mean	sd
1	0.05	2	2155.0	3273.4	3240.0	0.0717
2	0.11	4	1615.0	2155.0	1760.0	0.0257
3	0.27	10	1485.0	1615.0	1570.0	0.0128
4	0.64	25	1360.0	1485.0	1420.0	0.0103
5	0.77	30	1250.0	1360.0	1310.0	0.0106
6	1.77	69	1100.0	1250.0	1170.0	0.0142
7	3.94	153	968.5	1100.0	1040.0	0.0153
8	1.87	72	862.3	968.5	908.0	0.0142
9	1.23	48	811.0	862.3	831.0	13.3
10	4.14	161	722.0	811.0	766.0	25.9
11	11.39	442	635.0	722.0	676.0	26.3
12	16.75	650	504.5	635.0	573.0	36.5
13	26.36	1023	357.0	504.5	424.0	41.9
14	23.10	896	231.0	357.0	298.0	38.3
15	5.68	220	124.0	231.0	180.0	30.2
16	1.94	75	5.0	124.0	59.5	34.3

Ce ppm

Sub-pop	%	N	from	to	mean	sd
1	0.18	4	254.5	2.0	268.0	0.01240
2	0.22	5	216.0	254.5	233.0	0.02040
3	0.40	9	193.0	216.0	206.0	0.01390
4	1.98	44	176.5	193.0	184.0	0.00981
5	4.38	97	152.5	176.5	165.0	0.01650
6	0.75	17	143.53	152.5	148.0	0.00587
7	0.53	12	139.0	143.53	141.0	1.0700
8	3.34	74	120.5	139.0	130.0	4.6400
9	12.35	273	98.25	120.5	108.0	6.3200
10	21.36	472	75.5	98.25	87.9	6.4900
11	41.59	920	44.8	75.5	58.9	8.6000
12	11.67	258	26.55	44.8	37.1	5.3900
13	1.12	25	11.63	26.55	20.3	3.2600
14	0.13	3	4.34	11.63	6.49	1.5300

Appendix 5. Summary of Cr, La, Ni, Rb, Sr and Zr sub-populations and its statistical estimates, isolated by probability graphs modeling. The underscored values indicate that the probability graph, or part of it, was modeled with log transformed values.

Cr ppm						
Sub-pop	%	N	from	to	mean	sd
1	0.85	31	665.500	2000.000	994	0.0813
2	1.49	55	303.500	665.500	431	0.0885
3	7.23	267	158.000	303.500	214	0.0870
4	23.45	864	77.300	158.000	110	0.0974
5	5.12	189	60.000	77.300	71.5	0.0208
6	7.24	267	48.100	60.000	59.2	0.0280
7	6.64	245	43.650	48.100	48.7	0.0261
8	6.21	229	34.450	43.650	38.9	0.0272
9	5.10	188	30.900	34.450	32.7	0.0121
10	4.86	179	26.350	30.900	28.6	0.0167
11	3.34	123	23.550	26.350	24.8	0.0125
12	23.91	882	6.140	23.550	12.9	0.1550
13	2.65	98	2.755	6.140	4.11	0.0819
14	1.92	71	0.500	2.755	1.28	0.1600

La ppm						
Sub-pop	%	N	from	to	mean	sd
1	0.08	3	234.000	388.000	383.00	0.0837
2	0.09	4	150.000	234.000	178.00	0.0338
3	0.31	12	113.500	150.000	130.00	0.0285
4	0.58	22	100.500	113.500	107.00	0.0133
5	2.95	114	88.450	100.500	93.70	0.0157
6	3.17	122	75.050	88.450	81.80	0.0203
7	1.07	41	70.115	75.050	72.80	0.0084
8	2.29	88	60.450	70.115	64.700	2.3500
9	7.20	278	50.950	60.450	55.500	2.6800
10	13.26	511	42.750	50.950	47.000	2.4200
11	12.93	499	34.700	42.750	38.900	2.2400
12	18.63	718	26.000	34.700	30.000	2.5200
13	28.21	1088	16.050	26.000	21.100	2.9600
14	8.46	326	7.945	16.050	12.500	2.2200
15	0.77	30	2.000	7.945	5.260	1.2900

Ni ppm						
Sub-pop	%	N	from	to	mean	sd
1	0.93	36	281.50	870.00	472	0.1180
2	0.28	11	180.00	281.50	212	0.0672
3	0.15	6	160.00	180.00	170	0.0162
4	0.34	13	120.50	160.00	139	0.0345
5	2.70	104	90.15	120.50	104	0.0337
6	10.03	386	66.20	90.15	76.3	0.0387
7	27.73	1066	43.00	66.20	53.5	0.0540
8	18.05	694	30.65	43.00	36.5	0.0419
9	11.98	461	22.15	30.65	26.3	0.0372
10	2.22	85	18.55	22.15	20.1	0.0203
11	4.58	176	10.13	18.55	13.3	0.0649
12	19.80	761	3.23	10.13	5.84	0.1260
13	0.98	38	1.50	3.23	2.25	0.0755
14	0.23	9	1.00	1.50	1.01	0.0720

Rb ppm						
Sub-pop	%	N	from	to	mean	sd
1	0.09	3	279	394	340.0	0.0516
2	0.57	22	244	279.5	265.0	0.0203
3	0.62	24	229	244	238.0	0.0087
4	4.71	181	195	229	212.0	0.0180
5	2.43	94	172.5	195	183.0	0.0141
6	3.92	151	156	172.5	164.0	0.0127
7	1.97	76	139	156	147.0	0.0144
8	1.88	72	120.78	139	131.0	0.0152
9	2.36	91	106.5	120.78	112.0	3.470
10	5.89	227	85.5	106.5	97.2	5.470
11	6.17	238	60.1	85.5	71.7	6.510
12	12.49	482	44.8	60.1	52.7	4.400
13	50.07	1931	15.3	44.8	29.9	7.880
14	6.63	256	6.595	15.3	11.7	2.350
15	0.21	8	2	6.595	3.05	1.570

Sr ppm						
Sub-pop	%	N	from	to	mean	sd
1	0.21	8	1040	1125	1080.0	0.0084
2	0.18	7	947	1040	990.0	0.0111
3	0.29	11	894	947	921.0	0.0073
4	0.72	28	852	894	872.0	0.0063
5	1.80	69	768.5	852	810.0	0.0123
6	0.82	32	718.5	768.5	742.0	0.0085
7	1.61	62	652.5	718.5	685.0	0.0115
8	0.95	36	608.06	652.5	630.0	0.0087
9	0.82	32	545.5	608.06	584.00	14.500
10	17.73	684	401	545.5	464.00	35.900
11	16.59	640	319	401	362.00	23.900
12	15.28	589	235	319	275.00	24.600
13	23.12	892	166	235	203.00	20.500
14	11.54	445	121	166	145.00	12.700
15	7.52	290	73.1	121	97.30	12.800

Zr ppm						
Sub-pop	%	N	from	to	mean	sd
1	0.05	2	946	1278	1270	0.04130
2	0.15	6	773.5	946	814	0.00667
3	0.25	10	697	773.5	728	0.00939
4	3.25	127	610	697	653	0.01410
5	2.44	95	560	610	584	0.00858
6	0.32	13	522	560	541	0.00706
7	0.15	6	508	522	513	3.640
8	0.48	19	461	508	485	12.300
9	1.54	60	360	461	409	26.100
10	11.30	440	303	360	330	16.400
11	27.13	1058	215	303	260	24.500
12	52.11	2031	73.8	215	152	33.000
13	0.82	32	5	73.8	36.1	12.700

Appendix 6. Summary of Y sub-populations and its statistical estimates isolated by probability graphs modeling. The underscored values indicate that the probability graph was modeled with log transformed values.

			Y ppm			
Sub-pop	**%**	**N**	**from**	**to**	**mean**	**sd**
1	0.08	3	337.000	1001.112	773	0.1840
2	0.24	9	183.000	337.000	250	0.0683
3	0.58	22	120.500	183.000	146	0.0498
4	2.32	87	77.650	120.500	98.7	0.0519
5	10.02	376	55.300	77.650	64.7	0.0394
6	6.81	255	47.300	55.300	51.4	0.0174
7	27.77	1041	37.750	47.300	41.8	0.0266
8	31.04	1164	30.150	37.750	33.7	0.0290
9	13.65	512	25.750	30.150	27.8	0.0222
10	5.73	215	21.050	25.750	23.5	0.0252
11	1.08	40	18.500	21.050	19.8	0.0138
12	0.55	21	9.740	18.500	11.9	0.0546
13	0.13	5	7.000	9.740	8.3	0.0437