GEOCHEMICAL TRENDS OF THE NEOARCHEAN VOLCANISM (ITACAIÚNAS SUPERGROUP) IN THE CARAJÁS MINERAL PROVINCE (CMP), PA, BRASIL

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ABSTRACT

Since the pioneering work of Gibbs et al. (1986), highlighting a bimodal geochemical tendency for the volcanic rocks of the Parauapebas Formation (base of the Grão-Pará Group, Itacaiúnas Supergroup), many authors summarize, as bimodal, the Neoarchean volcanic activity manifested in the Carajás Basin (sensu lato). In this work, 155 (meta)volcanic rocks of the Itacaiúnas Supergroup; sampled throughout the basin; had their major and trace elements analyzed. The entire dataset was submitted to a Principal Component Analysis (PCA), which highlighted the main associations among 49 elements. This procedure validated lithogeochemical classification based on HFSE ratio diagrams and also gave some hints on the volcanic processes registered in the rocks. Our data set indicates that the volcanism of the Itacaiúnas Supergroup has a broad compositional spectrum, ranging from basic to acidic terms, but mostly intermediate ones. A subsequent lithogeochemical approach on the geochemical trends expressed in the (meta) volcanic rocks of the Itacaiúnas Supergroup may constrain some current ideas on the Neoarchean geotectonic evolution of the CMP.

KEY WORDS: Neoarchean Volcanism; Carajás; Itacaiúnas Supergroup; Lithogeochemistry.

INTRODUCTION

The Neoarchean volcanism of the Itacaiúnas Supergroup is distributed along 200 km (E-W) by 50 km (N-S) through the sigmoidal macrostructure of the Carajás Basin (sensu lato). The volcanic units of this supergroup have already been compared to continental toleiitic (*eg.,* Gibbs et al. 1986), shoshonitic (Dardenne et al. 1988) and calcalkaline andesitic (Teixeira and Eggler 1994) basalts. The main geochemical studies on the mafic (meta)volcanic rocks suggest them to be related to rift activity and crustal contamination processes. But, there is no consensus about the main rifting mechanism; if it is related (*eg*. Zuchetti 2007) or not (*eg.,* Gibbs et al. 1986) to subduction processes. Even recent studies supporting crustal contamination of the basalts of the Parauapebas Fm. (*eg*., Martins 2017), do not revoke the possibility of sub-continental lithosphere metasomatism in subduction zone.

We present a new dataset comprising 155 well-preserved (meta)volcanic rock samples of the undivided Itacaiúnas Supergroup (Fig. 01). The samples were collected from outcrops and drill-cores during systematic geological mapping at scale 1:100,000 (Tavares and Silva 2012; Tavares 2014; Justo and Lopes 2014; Oliveira 2018) and others (Costa et al. 2015), undertaken by the Geological Survey of Brazil together with a PhD research (Justo 2018).

METHODS

The fresh whole-rock samples were analyzed in the ALS-Chemex and SGS Geosol laboratories (Brazil). Major elements were measured by X-ray fluorescence (XRF), after alkaline fusion with lithium metaborate; Rare Earth Elements (REE) and other trace elements were dosed by ICP-MS, after alkaline fusion with lithium metaborate. PCA multivariate statistics, lithogeochemical and petrological studies were processed by the *Statistica* software. The petrographic characterization done under optical microscope is not addressed here.

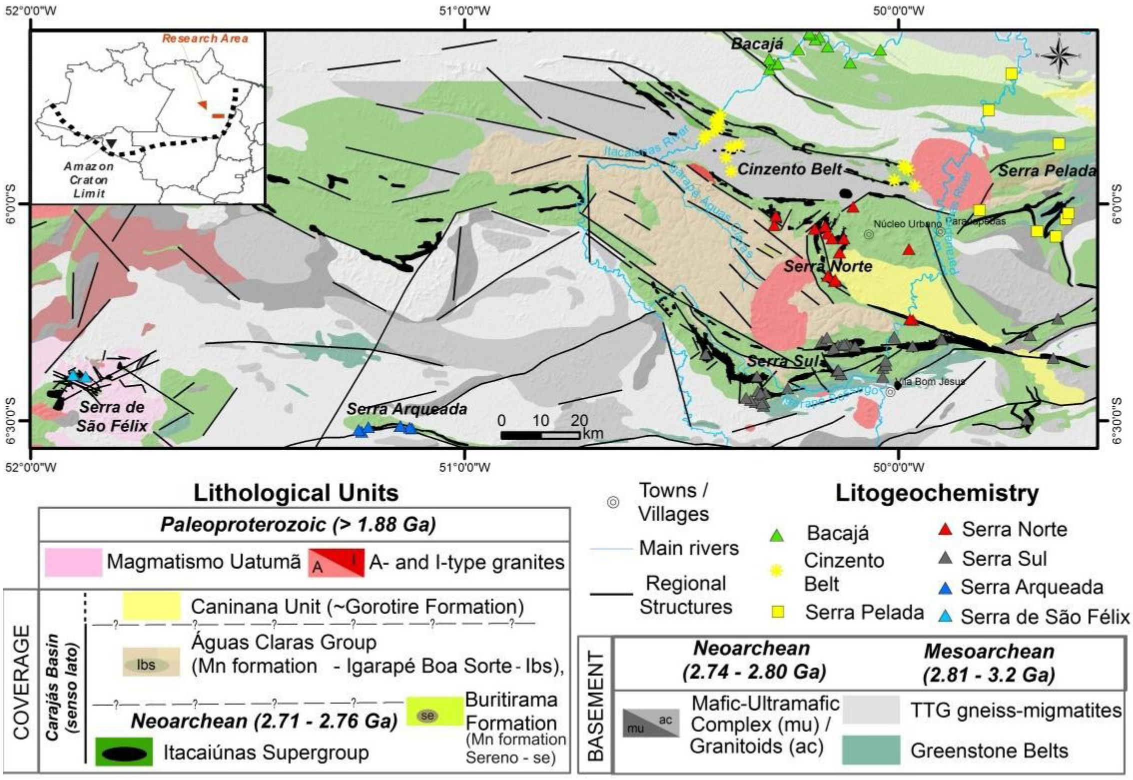

Figure 1 - Schematic geological map of the CMP (adapted from DOCEGEO 1988, Tavares and Silva 2012, Tavares 2014, Justo and Lopes 2014, Oliveira 2018 and Costa et al. 2015).

RESULTS AND DISCUSSION

The results of the PCA are shown in Table 01. The eigenvalues are presented for the first 14 principal components (PC), which accounts for more than 92% of the variation in the dataset (Table 01a). The R-mode loadings, shown for the first 3 PC, account for more than 65% of the data variation; the contribution of each of the 49 variables to each PC is shown in the Table 01b. These loadings are the eigenvectors scaled by multiply, in order, each of the eigenvector by the square root of the eigenvalues (Grunsky, 2007). Over 34% of the total data variation is represented by the PC1, where Y, REE, Zr, Nb, and Ga are mainly accounted by high negative correlation (< -0.7). Except by Ga, this high negative correlated association corresponds to the High Field Strength Elements (HFSE), a set of incompatible elements that present low mobility during most of the petrogenetic processes. Such high correlated association ensures the rock classification based on HSFE ratio diagrams (Fig. 02a). The PC2 accounts for more than 23% of the data variability, it shows high negative correlation among Mg, Sc, Ti, V, Cr, Mn, Fe, Co, Ni and Zn (< -0.7); while Th and U show positive correlation values (~ +0.7). The PC3 highlights a negative correlation among Ba, K_2O, Sr and Rb (~-0.7).

The sample scores between PC1 x PC2 are illustrated in Figure 02b, according to the volcanic rock classification based on HFSE ratios (Figure 02a); and the score of the variables (elements) are indicated by their chemical symbols. The positive side of PC2 concentrates the basic volcanic rocks and shows affinity to Mg and to a set of compatible elements, such as Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn and especially Cu; what puts the basic rocks as an important potential source of the copper mineralization found throughout the province. These basic rocks do not show correlation to other incompatible elements such as K, Rb, U and Th; which are typically associated to acid volcanic rocks and heterogeneously distributed through the 2 negative side of PC2. Compared to the HFSE; K, Rb, U and Th tend to show higher mobility in reacted fluids. The acid rocks are richer in the REE than the basic rocks; and the latter are less enriched in light REE (LREE) relative to heavy REE (HREE), if compared to the former.

Table 1 - PCA's results: a) eigenvalues for the first 14 PCs; b) R-mode loadings of the first 3 PCs for positive (blue) and negative (red) values and over 70% of correlation (bold).

a)

PCs	Eigenvalue	Total (%)	Cumulative (%)
PC 1	**17.00**	**34.70**	**34.70**
PC 2	**11.55**	**23.56**	**58.26**
PC 3	**3.41**	**6.95**	**65.21**
PC 4	2.62	5.34	70.55
PC 5	2.19	4.48	75.02
PC 6	1.53	3.13	78.15
PC 7	1.38	2.82	80.96
PC 8	1.22	2.50	83.46
PC 9	0.99	2.01	85.48
PC 10	0.85	1.74	87.21
PC 11	0.74	1.52	88.73
PC 12	0.63	1.28	90.01
PC 13	0.56	1.13	91.14
PC 14	0.49	1.00	92.14

b)

Major	PC 1	PC 2	PC 3	Traces	PC 1	PC 2	PC 3	Traces	PC 1	PC 2	PC 3	Traces	PC 1	PC 2	PC 3
SiO_2	0.42	**-0.80**	-0.07	Be	-0.56	-0.41	-0.26	Mo	-0.06	-0.21	0.00	Dy	**-0.95**	0.01	0.15
TiO_2	-0.50	**0.69**	-0.01	Sc	-0.32	**0.86**	-0.02	Ag	-0.21	0.53	0.11	Ho	**-0.94**	0.03	0.18
Al_2O_3	-0.61	0.38	-0.32	V	-0.22	**0.90**	-0.03	In	-0.34	0.56	0.04	Er	**-0.93**	0.03	0.19
Fe_2O_3t	-0.51	**0.72**	0.20	Cr	-0.08	**0.82**	0.01	Sn	-0.22	-0.50	0.11	Tm	**-0.91**	0.05	0.19
MnO	-0.35	**0.70**	0.14	Co	-0.43	**0.77**	-0.01	Cs	-0.41	-0.16	-0.32	Yb	**-0.92**	0.01	0.17
MgO	-0.40	**0.79**	0.08	Ni	-0.09	**0.88**	-0.05	Ba	-0.44	-0.08	**-0.75**	Lu	**-0.89**	0.01	0.18
CaO	-0.26	0.62	-0.45	Cu	0.03	0.33	-0.16	La	**-0.69**	-0.49	0.00	Hf	-0.54	-0.36	0.06
Na_2O	0.04	0.14	-0.63	Zn	-0.42	**0.70**	-0.01	Ce	**-0.73**	-0.48	-0.02	Ta	-0.49	-0.25	0.12
K_2O	-0.38	-0.29	**-0.73**	Ga	**-0.71**	0.19	-0.26	Pr	**-0.75**	-0.47	-0.03	W	-0.16	-0.20	0.08
				Rb	-0.39	-0.30	**-0.67**	Nd	**-0.78**	-0.41	-0.01	Pb	-0.39	0.10	-0.07
				Sr	-0.15	0.32	**-0.71**	Sm	**-0.83**	-0.35	0.05	Th	-0.42	**-0.74**	-0.05
				Y	**-0.93**	0.05	0.20	Eu	**-0.80**	0.14	-0.01	U	-0.39	**-0.69**	0.08
				Zr	**-0.69**	-0.34	0.05	Gd	**-0.93**	-0.14	0.09				
				Nb	**-0.72**	-0.49	0.02	Tb	**-0.96**	-0.06	0.10				

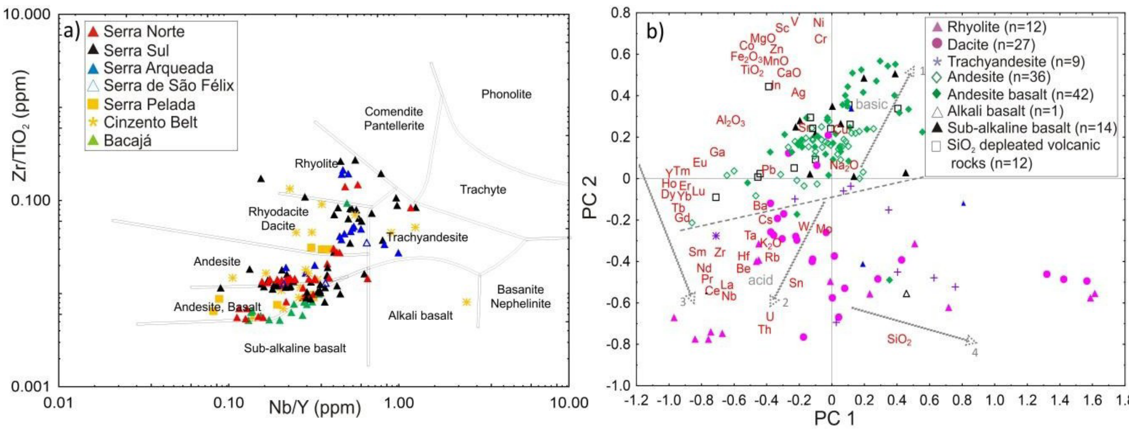

Fig. 2 - a) Nb/Y vs. Zr/TiO_2 diagram for volcanic rocks (Winchester and Floyd 1977); b) PC1 x PC2 scatterplot based on the 49-element log-centered lithogeochemical data of the volcanic rocks; element enrichment trends as gray arrows: [1]basic rocks, [2]acid rocks, [3]REE, [4]SiO_2.

The andesitic basalts constitute the largest group of the sampled rock types (42 samples). Their REE+Y and HFSE patterns summarized on multi-element diagrams (Fig.3ab) are remarkably coherent. They are characterized by variable LREE enrichment relative to HREE, quantified as $(La/Yb)_{CN}$ ratios ranging 1-9; and by expressive Nb and Ta depletions.

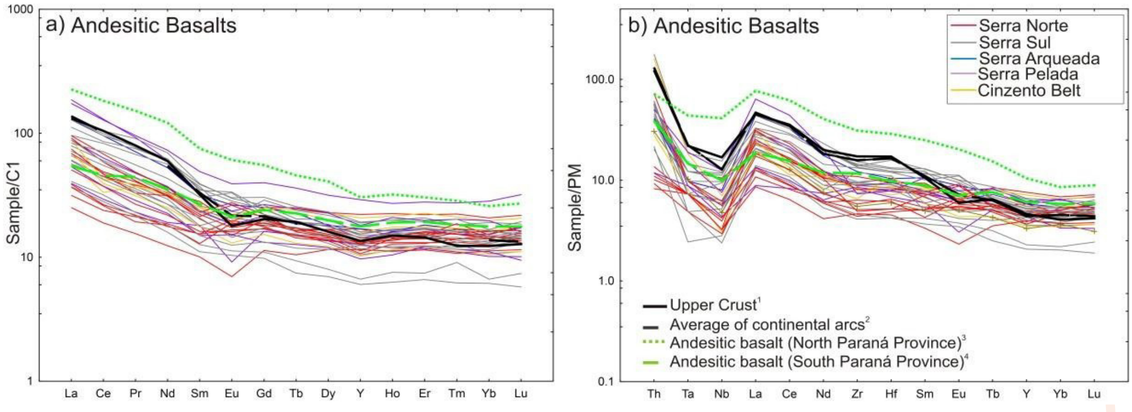

Fig. 3 - a) REE+Y chondrite (Anders and Grevesse, 1989) normalized and b) HFSE primitive mantle (Sun and McDonough, 1989) normalized diagrams for andesitic basalts. Sources: [1]Rudnick and Gao (2003); [2]Condie and Kröner (2013); [3]Baggio et al. (2018); [4]De Min et al. (2018).

CONCLUSIONS

The chemical diversity of the Neoarchean volcanism in the Carajás Basin appears to be a primary feature, locally assigned to post-magmatic events (*eg.,* Cinzento Belt). The high correlation shown by the "immobile" HFSE indicates that some of the original geochemical characteristics of the volcanic rocks are still partially preserved. The LREE enrichment relative to HREE and the distinctive trace element patterns observed in the andesitic basalts, particularly the Nb-Ta depletion, suggest that the volcanic activity was not only controlled by mineral-melt processes. Possibly, the volcanic activity had the contribution of element fractionation during partitioning between hydrous fluids removed from a subducting slab and the residual solid. A degree of crustal contamination can also be related to the Itacaiúnas Supergroup volcanism, due to the general similarity shown by the trace element patterns of such environments. A more robust geotectonic understanding of the Neoarchean volcanism in the CMP requires extra mineral and isotopic chemistry data to track its magmatic reservoirs.

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