



## ANÁLISIS DE LA METEORIZACIÓN QUÍMICA Y PROVENIENCIA EN LATERITAS SUBTROPICALES DE MISIONES

### PROBING INTO THE NATURE OF CHEMICAL WEATHERING AND PROVENANCE IN MISIONES SUBTROPICAL LATERITES

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#### Abstract

*Subtropical laterites in Misiones province cover the Jurassic-Cretaceous Serra Geral basalts. Two hypotheses have been proposed to explain the origin of these laterites. The autochthonous theory states that these deposits result from chemical weathering of the underlying tholeiitic basalts. However, during the last decade, an allochthonous “tropical loess” model was proposed. A lateritic profile (~2 m thick, 26°9'58"S - 54°35'3"W) was analyzed in order to constrain the nature of weathering processes and the provenance of the lateritic layer. Different alteration indices showed the extreme leaching of the basaltic bedrock. The index of lateritization (IOL = 35-50) and the accompanying SAF ternary plot (SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>), indicate an increasing weathering trend towards the profiles' top, reflecting the modest loss of SiO<sub>2</sub> (relative to Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>) during kaolinitization. The geochemical approach used in this work clearly relates the analyzed laterites to the underlying tholeiitic basalts, supporting the autochthonous origin theory.*

**Keywords:** tropical/subtropical weathering, weathering indices, Serra Geral Fm., lateritic sources.

#### Introduction

Laterites are widely distributed worldwide in the tropical/subtropical belt between 20°N and 28°S. These red or yellowish-red materials, where all mobile elements have been removed, are relatively enriched in iron and aluminum oxides, and are developed over iron-containing parent rocks, such as basalts. In South America's Paraná Basin, laterites blanket the Serra Geral basalts, which are among the largest known volcanic features in the world and they are dominant in Misiones province. A subtropical humid climate characterizes the region, with a lack of a dry season; mean annual temperature is ~21°C. Mean annual rainfall reaches ~1700 mm in the south of Misiones province and increases up to ~2000 mm in the north (Morrás et al., 2009).

The origin of the laterites of Misiones was traditionally ascribed to the intense chemical weathering of the tholeiitic basalts. However, during the last decades, a heterodox origin was also suggested for these laterites, as well as for those of SE Brazil, E Paraguay, N Uruguay and the lowlands of Bolivia. In this sense, Iriondo and Kröhling (1997; 2007) defined the allochthonous “tropical loess” model. These authors argued, based on grain-size and mineralogy, that the tropical loess was generated by the accumulation of silt-sized particles and aggregates mainly deflated from the alluvial plains of Paraná, Paraguay and Uruguay rivers during the Last Glacial Maximum. They proposed that after the dust accumulation, a savanna environment was established in the region, promoting the mobilization and percolation of iron, forming concretions of iron sesquioxides. Conversely, Morrás et al. (2009) argued on behalf of the autochthonous origin of Misiones' laterites, using different analytical techniques and discussing in particular the presence of gravelly levels named “stone lines”. They described two types of stone lines in Misiones' lateritic profiles. One was defined as ferruginous nodular horizons, mainly composed of iron nodules (hematitic, goethitic and intermediate nodules), resulting from in situ weathering and glaebulization processes of the underlying basalt. The second type is composed of siliceous horizons, interpreted as the in situ relicts of pre-existing

quartz veins in the basalt. These stone lines were previously interpreted by Iriondo and Kröhling (2007) as an allochthonous feature that suggests an unconformity that would reveal aridization that promoted erosion and sedimentary processes during the Last Glacial Maximum and the Holocene. The aims of this work are: 1) to assess the intensity of weathering processes in this subtropical region; and 2) to add substantial evidence to constrain the origin of Misiones' laterites.

### Materials and Methods

A ~2 m thick lateritic weathering profile located ~60 km south of Puerto Iguazú (Misiones province, 26°9'58"S - 54°35'3"W) was sampled for geochemical analyses. In this region, the lateritic layer is several meters thick, but complete profiles that include exposed fresh and the whole sequence of lateritic layer are rarely found. The analyzed samples, from the base to the top of the profile are: MIS-05, MIS-04, MIS-03, MIS-02 and MIS-01 (Table 1). Major oxides and trace elements were determined by ICP-OES and ICP-MS. The Chemical Index of Alteration (CIA; Nesbitt and Young, 1982), the Mafic Index of Alteration (MIA; Babechuk et al., 2014), and the Index of Lateritization (IOL; Babechuk et al., 2014) were calculated for the lateritic profile and Serra Geral basalts.

### Results

Most igneous rocks have CIA values that range between 35 and 50, and mafic rocks exhibit the lowest values (Babechuk et al., 2014). Similar to other basalts, the basaltic bedrock (MIS-05) shows a CIA of ~37 (Table 1). The CIAs increase from the bedrock to the top of the profile, reaching the most altered laterite sample (MIS-01) a value of ~99. The high CIAs observed in the uppermost samples MIS-02 and MIS-01 indicate that mobile elements were removed almost completely from these layers. In most cases, the MIA values are close to the CIAs (Table 1), and both indices are significantly correlated ( $r^2 = 0.98$ ,  $p < 0.001$ ) in the lateritic profile, evidencing the similar bulk weathering behavior of Mg, Ca and Na. The intermediate level (MIS-03) exhibits the largest difference between both indices (Table 1), which could indicate a slightly different behavior of Mg compared to Ca and Na during clay formation in the intermediate weathering stages, as it was suggested by Babechuk et al. (2014).

Table 1. Weathering indices of the studied lateritic profile. Data of Serra Geral basalts are also included: Basalt<sup>1</sup> from Rocha Junior et al. (2013; n = 10) and Basalt<sup>2</sup> from Peate and Hawkesworth (1996; n = 26).

|     | Lateritic profile |        |        |        |        | Serra Geral basalts |                     |
|-----|-------------------|--------|--------|--------|--------|---------------------|---------------------|
|     | MIS-05            | MIS-04 | MIS-03 | MIS-02 | MIS-01 | Basalt <sup>1</sup> | Basalt <sup>2</sup> |
| CIA | 37.5              | 47.9   | 69.6   | 98.8   | 99.9   | 38.3                | 38.5                |
| MIA | 37.4              | 45.7   | 61.1   | 96.0   | 99.0   | 40.5                | 38.7                |
| IOL | 35.2              | 37.0   | 43.7   | 52.0   | 55.0   | 36.2                | 34.1                |

Since the dominant process occurring during lateritization is desilication, the IOL index, which includes the Si, was calculated in the lateritic profile, and the SAF ternary diagram that accompanies this index is shown in Figure 1A. The limit of kaolinitization for the basalts of Misiones, calculated from sample MIS-05 is 44.3% SiO<sub>2</sub> and in terms of IOL it occurs at an IOL = 55.7. The IOL values calculated for the lateritic profile range between 35 and 55 (Table 1), with an increasing trend towards the top of the profile, consistent with the modest SiO<sub>2</sub> loss, relative to Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> during kaolinitization (Babechuk et al., 2014). In this sense, all laterite samples plot within the field of kaolinitization, and a trend of increasing weathering is observed from the base to the top of the profile. Besides, the uppermost sample of the profile (MIS-01) plots close to the boundary of the weak lateritization field.

Several compositional diagrams have been proposed in the literature to identify the sources of sediments and sedimentary rocks (e.g., Roser and Korsch, 1986), as well as to constrain the provenance of dust, soils and loess-paleosol sequences (e.g., Babeesh et al., 2017). Plots

involving trace elements have proven to be more useful to identify the sources (e.g., Campodonico et al., 2016). Figure 1B and C show the La-Th-Sc triangles for the laterite samples. Loess from Argentina, suspended sediments from the Middle Paraná and Uruguay rivers, and Serra Geral basalts from Brazil are included for comparison. The laterite samples and the Serra Geral basalts plot in the oceanic island arc field, whereas the loess samples and the suspended sediments cluster around the field of continental arc, which encompasses a wide compositional range of igneous rocks (i.e., from granitic to basaltic, Fig. 1B). Figure 1C shows that laterite samples, the Serra Geral basalts and the Uruguay River suspended sediments preserve the signature of metabasic sources, whereas the loess and Middle Paraná River suspended load reflect a mixed origin. This evidences that the particulate matter from the Middle Paraná River does not preserve a tholeiitic signature and is mainly supplied by the Andean tributaries (i.e., Bermejo and Pilcomayo rivers; Campodonico et al., 2016).

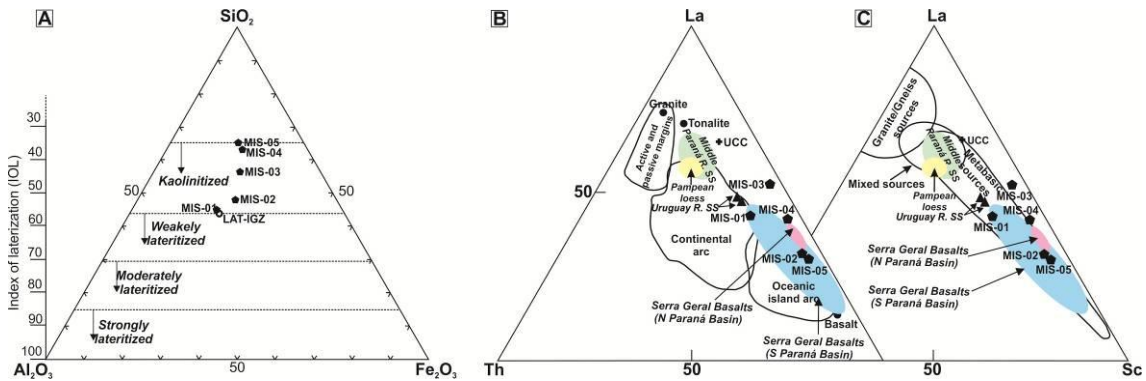


Figure 1. A) SAF ternary diagram for the lateritic profile. B) and C) La-Th-Sc ternary diagrams illustrating the tectonic setting composition and sources of the lateritic profile. Compositional fields of Pampean loess (Gallet et al., 1998; Nicolli et al., 2010; Borgnino et al., 2013; Pasquini et al., 2017); Serra Geral basalts of the South (Peate and Hawkesworth, 1996) and North (Rocha-Júnior et al., 2013) portions of Paraná Basin; and Middle Paraná (Campodonico et al., 2016) and Uruguay (Depetris and Pasquini, 2007) rivers suspended sediments (SS) are included for comparison.

Figure 2 shows the bivariate diagram MIA vs. ICV, where the lines of the theoretical evolution of Serra Geral basalts and a mean Andean andesite (<http://www.geokem.com>) are also included. The lowermost (MIS-05 and MIS-04) and the intermediate (MIS-03) laterite samples plot over the Serra Geral basalts line, whereas the uppermost samples (MIS-02 and MIS-01) exhibit a higher degree of chemical weathering. Likewise, the suspended sediments of the Uruguay River plot over the Serra Geral basalts line, reflecting the signature of its sources. Conversely, the Middle Paraná River suspended load and the Pampean loess cluster around the theoretical Andean andesite evolution line, indicating that they preserve the weathering imprint of their source.

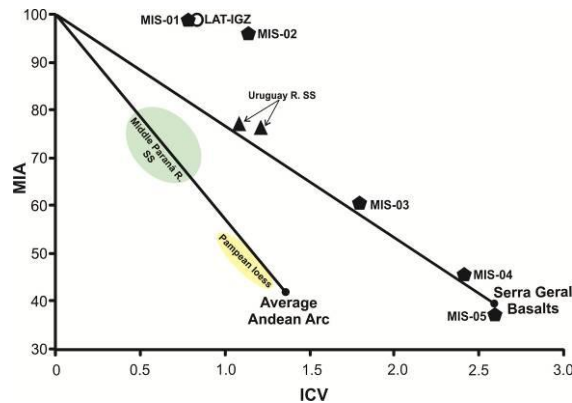


Figure 2. MIA vs. ICV plot for samples of the lateritic profile. The theoretical evolution of the Serra Geral basalts (mean composition from Peate and Hawkesworth, 1996 and Rocha-Júnior et al., 2013) and the Andesitic Andean Arc (AAA, <http://www.geokem.com>) are also included. Suspended sediments from Paraná and Uruguay rivers, as well as Pampean loess are plotted for comparison (references in Fig. 1).



## Conclusions

Geochemical data of a subtropical lateritic profile in Misiones province was used to establish the intensity of weathering processes, as well as to constrain the origin of such laterites. Weathering indices (i.e., CIA, ICV, MIA) confirm the progressive chemical alteration of the basaltic bedrock towards the top of the profile. The index of lateritization (IOL) and the accompanying SAF ternary plot indicate that the trend of increasing weathering from the base to the top of the lateritic profile (IOL values from 35 to 55) is consistent with the modest loss of  $\text{SiO}_2$  (relative to  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ ) during kaolinitization. Geochemical tools (i.e., compositional diagrams, bivariate plot MIA vs. ICV) clearly associate the analyzed laterites with the underlying tholeiitic basalts. The laterites do not preserve an Andean signature as the Middle Paraná River suspended sediments do. Paraná's alluvial plain was pointed out as the source area of the deflated sediments in the tropical loess hypothesis. Thus, data presented in this study supports further the autochthonous origin, contesting the theory that such laterites result from the extreme chemical weathering of tropical loess.

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