

Thermal Infrared Spectroscopy and Geochemical Analyses of Volcanic Rocks from the Paraná Basin (Brazil)

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Abstract

The current stratigraphy of volcanic rocks from the Paraná Basin is based mainly on whole rock geochemical analyses, which allow the subdivision of the basalt flows in high-TiO₂ and low-TiO₂ rocks. The work aims to find thermal infrared spectral signatures of the volcanic rocks that correlate with their geochemical signatures. For this, eleven samples were analyzed by FTIR to identify the spectral signature of the basalts and dacites. After that, thin sections of every sample were analyzed. The petrographic, geochemical and spectroscopic data show comparable results. Samples with high TiO₂ values contain ilmenite and titanomagnetite, whereas the low-TiO₂ rocks contain only titanomagnetite as main Ti-bearing phase. Titanomagnetite and ilmenite show distinct spectral signatures in the thermal infrared. However, spectral signatures of the rock samples are complicated by overlapping spectral signatures of the single mineral components. The more coarse crystalline samples allow a better separation of the single components when compared to the more fine crystalline samples. The preliminary results suggest that there may be scope to develop thermal infrared spectroscopy as a faster method for lithostratigraphic classification of rocks from the Paraná Basin and other volcanic suites worldwide.

Introduction

The Paraná continental basaltic flood province covers an area of approximately 1.2 million km² (Figure 1) and represents a very important volcanic Province related to the Parana-Etendeka event, with 0.8x10⁶ km³ of lava flows. It was formed during the opening of the South Atlantic Ocean in the Early Cretaceous (Peate et al., 1992).

These rocks are basalts and dacite to rhyolite (Figure 2). The bimodality is given by the difference of SiO₂ content: for basalts around 52 wt% and dacite ca. 68 wt%.

Two magmatic mafic groups have been identified, according to their chemical characteristics (Melfi et al., 1988; Peate et al., 1992):

(1) a low-TiO₂ (< 2% wt.) group as the Gramado, the Esmeralda and the Ribera magmatic series and

(2) a high-TiO₂ (>2% wt.) group named Pitanga, the Paranapanema and the Urubici. The Caxias Formation is related to the Palmas acidic volcanic type, relatively poor in TiO₂ (and incompatible elements) and usually associated with low-TiO₂ basalts.

The main objective of this paper is to identify and differentiate these groups of rocks on the base of their thermal infrared spectra. To achieve this, eleven samples were selected: six belonging to the Paranapanema Formation (high-TiO₂ group) and five from the Caxias and Gramado Formations (low-TiO₂ group).

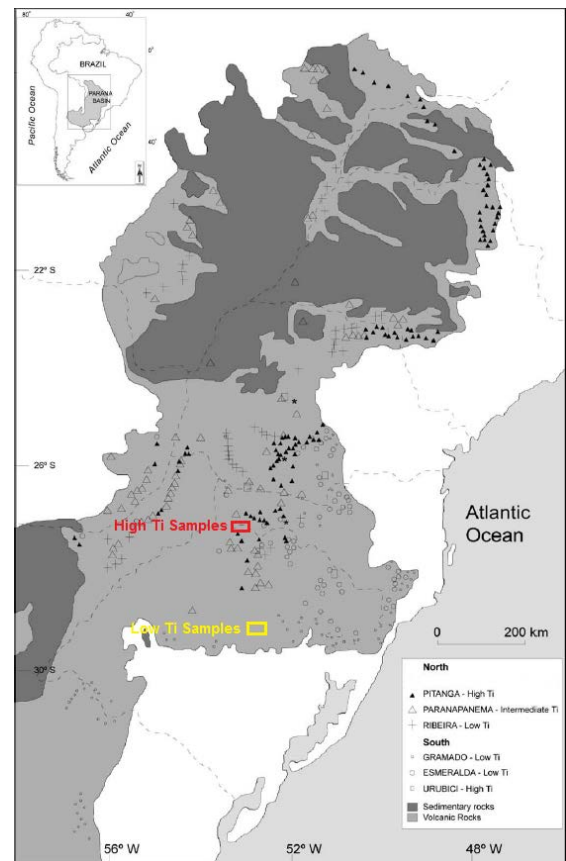


Figure 1: Map of the distribution of volcanic rock types in the Paraná Basin (Schenato et al., 2003). The studied samples belong to Paranapanema Formation (red square) and to the Caxias and Gramado Formations (yellow square)

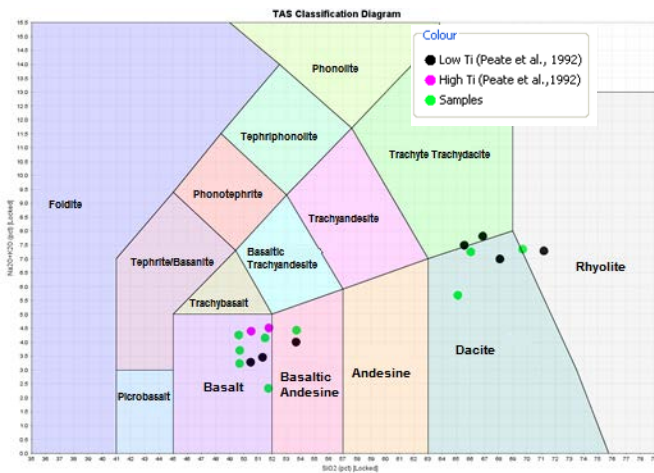


Figure 2: TAS (Total-Alkali vs. Silica) diagram of the Paraná Basin volcanic rocks utilizing the geochemical data from Peate et al. (1992) and from the samples used for this study.

Method

Eleven samples from the Paraná Basin were selected (from both TiO₂ groups) to be studied at the ARRC (Australian Resources Research Centre) of CSIRO (Commonwealth Scientific and Industrial Research Organization), Australia. They were first analyzed with the Bruker FTIR to identify the spectral signatures of the basalts and dacites, which contain feldspar, pyroxene and magnetite as major mineral phases.

One spectral property used as an indicator of mineral composition is known as the Christiansen frequency feature, which occurs in a wavelength region where the real part of the refractive index undergoes rapid change and thus may approach the refractive index of the medium surrounding the mineral grains, resulting in minimal scattering (Salisbury et al., 1989). Because this takes place at slightly shorter wavelengths than the fundamental molecular vibration, absorption is still relatively low. With little backscattering and little absorption, infrared radiation can pass through a sample relatively easily, resulting in a minimum in reflectance. The principal Christiansen Feature is associated with the strongest molecular vibration band and varied for different silicate minerals. This spectral feature, combined with the SCFM chemical index (the abundance of silica divided by the oxide abundances of Si, Ca, Fe, and Mg. $SCFM = SiO_2 / (SiO_2 + CaO + FeO + MgO)$) as suggested by Walter and Salisbury (1989), serves as a good indicator of the type of igneous rock.

Thin sections of every sample were also analyzed using thin section petrography, a scanning electron microscope (SEM) fitted with an EDAX energy dispersive spectrometer (EDS), as well as a Bruker Hyperion microscope connected to the FTIR.

The geochemical results were acquired by Santos et al. (2008) and Godoy et al. (in press).

Results

Representative results of two of the eleven analyzed samples will be presented here, one of high TiO₂ content and one of low TiO₂ content, for a better visualization.

In Figure 3, thermal infrared reflectance spectra are presented for a sample of high Ti (PD03) and low Ti (MM007). These are compared with three references curves obtained from the JPL (Jet Propulsion Laboratory) Spectral Library, showing the thermal infrared signature of quartz, feldspar and pyroxene. For all the spectra, the arrows indicate the location of the Christiansen Feature. We can observe that the wavelength position of the Christiansen feature shifts to lower wavelengths with higher SiO₂ content.

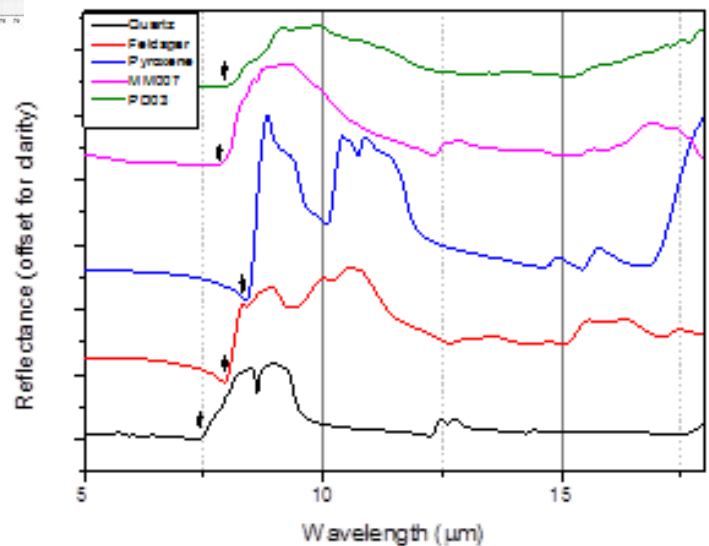


Figure 3: Reflectance spectra for a high TiO₂ sample (PD03, green), a low TiO₂ sample (MM007, pink), and for the reference silicate minerals (quartz, feldspar and pyroxene).

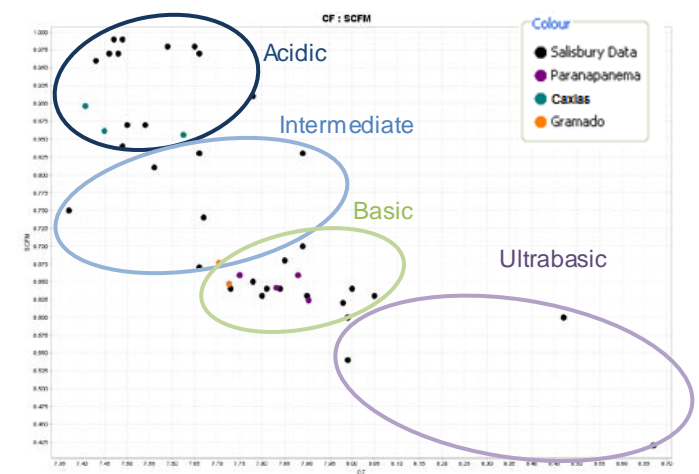


Figure 4: SCFM ($SiO_2 / (SiO_2 + CaO + FeO + MgO)$) vs. Christiansen Frequency (CF) for the samples belonging to Paranapanema Formation (high TiO₂) and for Caxias and Gramado Formation (low TiO₂).

Another way to visualize this result is presented in Figure 4 where the chemical index SCFM is plotted vs. the wavelength position of the Christiansen Feature. The classification is made on the basis of wt. % SiO₂ utilized by Salisbury *et al.* (1991) which are acidic (>63% SiO₂), intermediate (52-63% SiO₂), basic (45-52% SiO₂), and ultrabasic (<45% SiO₂). Again we can see that the higher the acidity of the rock, the lower the value of the wavelength position of the Christiansen feature.

From the petrographic analyses and the data acquired with the Bruker Hyperion microscope connected to the FTIR, it can be observed that samples with high TiO₂ values contain ilmenite (Figure 5a) and titanomagnetite (Figure 5b), whereas the low-TiO₂ rocks contain only titanomagnetite as main Ti-bearing phase (Figure 6). Also, the titanomagnetite belonging to the low TiO₂ samples have more FeO than the high TiO₂ ones.

Titanomagnetite and ilmenite show distinct spectral signatures in the thermal infrared, the pink spectrum in Figure 7 belongs to the titanomagnetite indicated in Figure 5a, and the red spectrum relates to the area of Figure 5b. The black spectrum belongs to the titanomagnetite of the low-TiO₂ sample, shown in Figure 6.

The three thermal infrared spectra were compared with ilmenite and magnetite spectra from the JPL Spectral Library. It can be seen that with increasing FeO content, the position of the Christiansen Feature shifts to higher wavelengths. The thermal infrared spectrum of sample PD03 (a), which has the highest Ti content, corresponds to the ilmenite reference spectrum (highest titanium content).

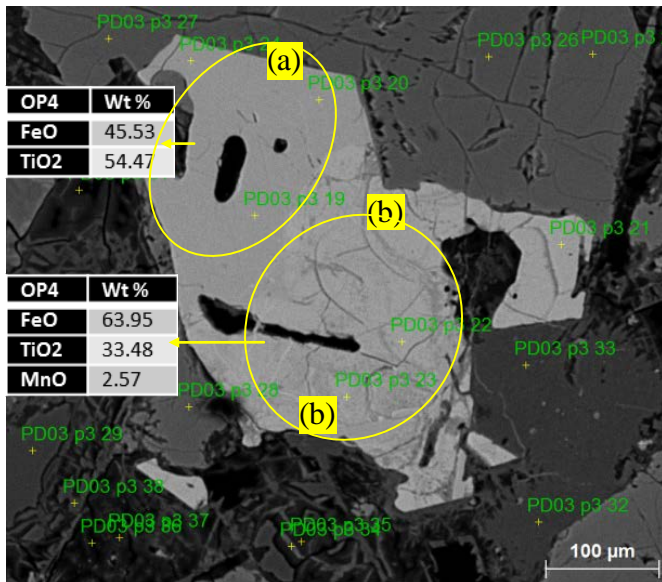


Figure 5: Ilmenite (a) and titanomagnetite (b) from high TiO₂ sample PD03 shown in the SEM image with their respective geochemical data

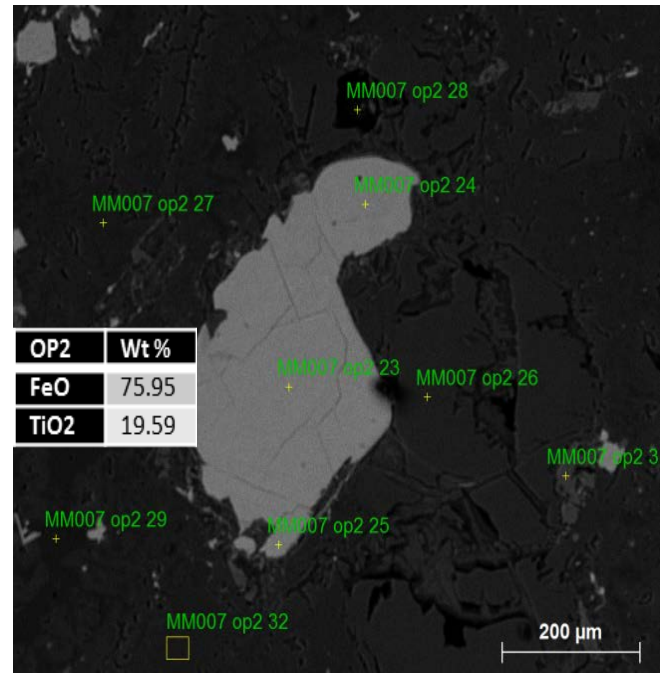


Figure 6: Opaque mineral belonging to one low TiO₂ sample. The image in the middle corresponds to the SEM image showing the titanomagnetite with the geochemical data.

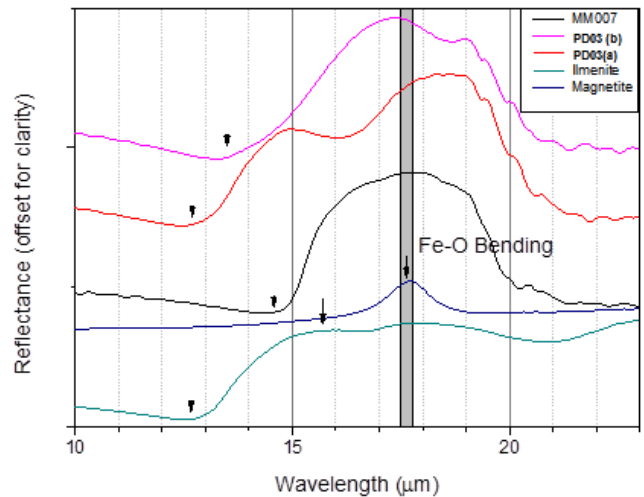


Figure 7: Thermal infrared spectra of the opaque minerals in the high TiO₂ samples (pink and red) and the low TiO₂ samples (black), compared with ilmenite and magnetite spectra from the JPL Spectral Library.

Conclusions

Eleven samples from Paraná Basin belonging to two different subdivisions (high TiO₂ and low TiO₂) were selected and analyzed to correlate their thermal infrared signatures with the geochemical data. The results show that the Christiansen Feature can be used to identify the rock type and estimate the SiO₂ content. Furthermore, we propose that the wavelength position of the Christiansen Feature of Fe-Ti-oxides, such as ilmenite, titanomagnetite and magnetite is correlated with their Fe/Ti ratio and that the thermal infrared spectra can be used to estimate the FeO and TiO₂ proportions in these opaque minerals.

However, further research about this is necessary, especially as spectral signatures of rock samples are complicated by overlapping spectral signatures of the single mineral components. The more coarse crystalline samples allow a better separation of the single components when compared to the more fine crystalline samples.

The results suggest that there may be scope to develop thermal infrared spectroscopy as a faster method for lithostratigraphic classification of rocks from the Parana Basin and other volcanic suites worldwide.

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