

Spectral reflectance and emissivity features of PO₄-bearing carbonatitic rocks from the Catalão I and Tapira complexes: New constraints for detection of igneous phosphates with remote sensing data

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Abstract. In order to determine the feasibility of conducting remote sensing of igneous phosphate rocks, reflectance and diffuse reflectance measurements were performed on eight samples from the Tapira and Catalão I Carbonatitic Alkaline complexes. Groundtruthing was performed with X-Ray Fluorescence and X-Ray Diffraction. Samples were collected from different parts of the weathering mantle until the bottom of the mine pits, showing better-preserved rock structure in this area. Samples were also dried and milled until 200mesh size. Reflectance measurements were made with an ASD Fieldspec 3 High-Resolution spectrometer in laboratory conditions. Diffuse Reflectance measurements were made with a FTIR Nicolet Nexus 6700 Spectrometer, and then Kirchoff's Law was applied to calculate emissivity. From the analyzed data, it can be observed that most samples that bear more than enough phosphate content to be mined show diagnostic REE absorption features in the VIS region of the spectra when the CaO/P₂O₅ ratio is higher than 1,0. However, mineralogical associations of phlogopite, vermiculite, calcite and dolomite in the SWIR region are significant in identifying the samples as carbonatitic rocks from the APIP. Also, emissivity results recorded a distinctive ν_3 broad absorption feature at 8,2 μ m for pure apatite from the Catalão I Complex and this absorption feature was consistently featured for the other samples studied. The results are in accordance with previous results obtained for other carbonatitic complexes in Mountain Pass (USA) and Kaneshin (AFG), for Carbonatitic Complexes with different ages.

Palavras-chave: carbonatite, rare earths elements, remote sensing, mineral exploration

1. Introduction

Phosphates, either from igneous or sedimentary rocks, are the primary constituents used in the fertilizer and biomedicine industry. However, their spectral characterization is sparse and insights on mineral exploration based on remote sensing quite scanty. Reference research for remote sensing of phosphate minerals can be found in Hunt *et al* (1972) and Clark (1999).

Spectroscopic research is critical for remotely sensed phosphate exploration. Amorer-Hernandez & Souza Filho (2012) and Cruz *et al* (2011) preliminary defined the spectral signatures of some Brazilian phosphate deposits. In this work, we show the spectroscopic features of phosphatic rocks from the Catalão I and Tapira Carbonatitic Alkaline complexes in the VNIR-SWIR-TIR region and identify the mineralogical associations that can be used as endmembers for remote sensing of igneous phosphates through multispectral and hyperspectral imagery.

2. Geological setting

The Catalão I and Tapira carbonatitic complexes are located in the Alto Paranaíba Igneous Province (Gibson *et al.* 1995), along with several other carbonatitic alkaline complexes (Serra Negra, Salitre I-II-III, Araxá). All these complexes are associated to a major tectonic structure with an 125° azimuth (Bizzi & Araújo 2005). These complexes were emplaced along deep northwest-trending faults related to the Alto Paranaíba cratonic arc, between the Paraná Basin and the São Francisco Craton (Gomes *et al* 1990). The syenites of the Catalão I complex yielded an age of 85.0 ± 0.9 Ma (Amaral *et al.* 1967; Sonoki & Garda 1988). The Tapira complex was formed at 81.7±7.9 Ma (Eby and Mariano 1992).

The main lithologies present in the complexes are dunite, clinopiroxenite, bebedourite, carbonatite and metasomatic phlogopitite (Brod *et al.* 2004). Feldspars and feldspathoids are

restricted to the fenites surrounding Catalão (Ribeiro 2008), whereas Tapira displays several sienitic intrusions (Brod 1999). Their regional location is displayed on figure 1.

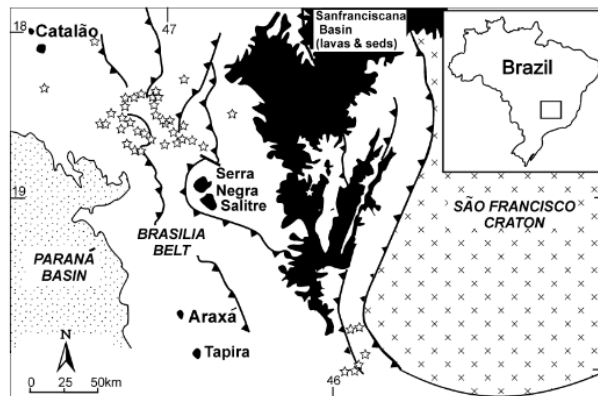


Figure 1 Geological sketch of the Alto Paranaíba Igneous Province. Catalão I is the northernmost complex and Tapira is located to the South (Source: Brod *et al.* 2002)

Several studies conducted on the Catalão I Complex focused on its weathering mantle. Oliveira & Imbernon (1998) defined five horizons from bottom to top:

Fresh rock: Phoscorites, phlogopitites and dunites, intruded by abundant carbonatites veins

Altered rock: In this horizon, rock structure is almost completely preserved. Metassomatic alteration can enrich phlogopitites with hydrothermally transported apatite (Toledo, 1999).

Isalteritic Sapprolite: A 25m deep profile, resulting from greater weathering of the altered rock. Some rock structure features are observed, but most mineral phases are homogenized in the horizon.

Aloteritic sapprolite: Another 25m deep profile. It has clayish-sandy material that can be yellow to reddish. Homogenization of mineral phases does not allow the identification of rock structure features.

Alloctonous covers: going from reddish to pink coloured soils.

ASTER images of the Catalão I and Tapira complexes displayed in figure 2. Mining operations of phosphates concentrate on the weathered mantle of both complexes. Ore phosphates (mainly apatite and less frequently aluminum phosphates) tend to be concentrated to the bottom of the pits at both complexes, just above the carbonatitic intrusions.

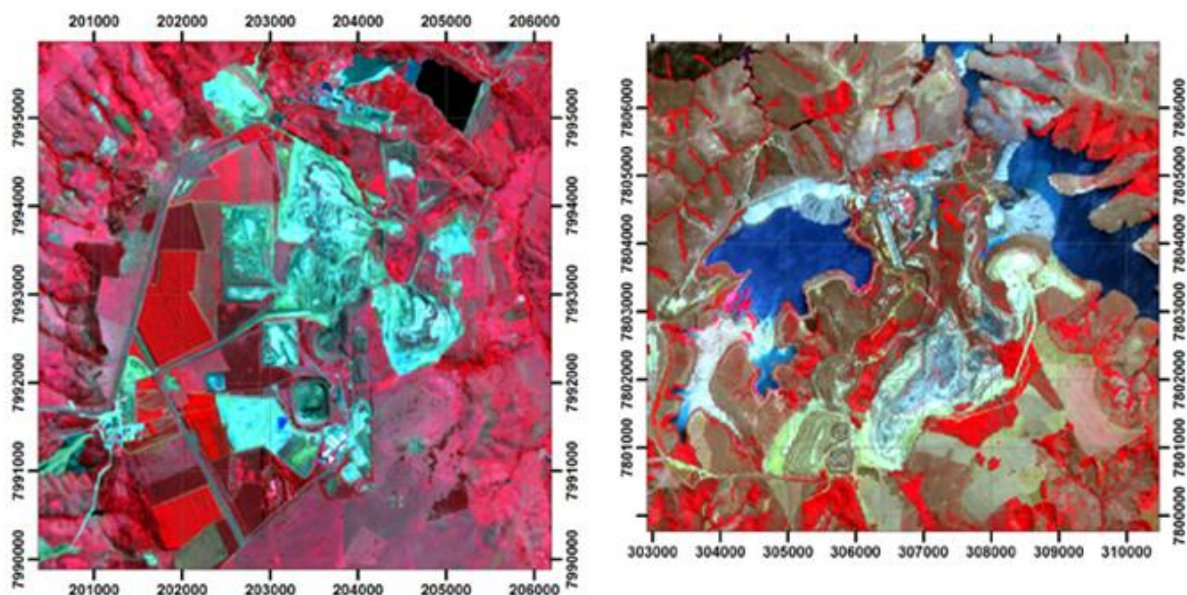


Figure 2. ASTER images (R3-G2-B1) of the Catalão I (left) and Tapira (right) complexes

3. Materials and methods

Samples collected from the Catalão I and Tapira carbonatitic alkaline complexes were dried for 24 hours at 50°C, milled at 200mesh size and then analyzed with an ASD Fieldspec 3 High-Resolution spectrometer. Equivalent samples were also analyzed on a FTIR Nicolet Nexus 6700 for Diffuse Reflectance and converted to emissivity using the Kirchoff's Law as shown in equation 1

$$\varepsilon=1-r \quad (1)$$

where r is diffuse reflectance. There has been some controversy regarding the accuracy of this formula for reflectance measurements not conducted on spectrometers with hemispherical reflectance. However, Vaughan *et al* (2003) indicate that measuring emissivity without an integrating sphere will not change the wavelength position of the absorption features, but only influence their depth.

The spectral results were cross-validated by XRD (using a Bruker AXS D2 diffractometer) and XRF (using a Phillips SW40 X Ray spectrometer) analyses.

The spectral libraries for each deposit were organized by lithotypes mapped in the field. Spectro-mineralogical classification was achieved by qualitative interpretation of continuum removed spectra, using the United States Geological Survey spectral library (Clark *et al.* 2007) and the G-MEX Spectral Library Handbook (Pontual *et al* 1997).

4. Results

Location of collected samples and their description are shown in table 1.

Table 1. Macroscopic description

X	Y	Sample	Sample Description
203652	7992866	CA-103	Cumulatic Carbonatite
202411	7992272	CA-123	Green Breccia with magnetite
202738	7992339	CA-130	Phlogopitite with magnetite
203943	7993343	CA-APCA	Apatite-Barite intergrowth
305999	7800656	TA-205	Vermiculite; Bebedourite with vermiculite
307160	7801575	TA-219	Breccia-carbonatite-B2 bebedourite contact
307754	7801906	TA-228A;	Altered B2 bebedourite with goethite
308096	7802571	TA-234	Isalterite with secondary phosphates

Reflectance spectra yielded from Catalão I samples (Figure 2) show that REE absorption features indicate the presence of the P-O ions on the analyzed material. This was also reported by Hunt *et al* (1972) for apatites of the Oka Carbonatite (Canada), linking this absorption features to ion charge transfer of the REE elements present in apatites as inclusions. These absorption features were also reported by Rowan *et al* (1986) for the Oka carbonatite, Iron Hill, Mountain Pass and Gem Park Complex (USA) and by Mars & Rowan (2011) for the Khanneshin Carbonatite (Afghanistan). REE absorption features are usually linked to goethite, phlogopite, calcite, dolomite and for altered phlogopitite lithotypes, with kaolinite.

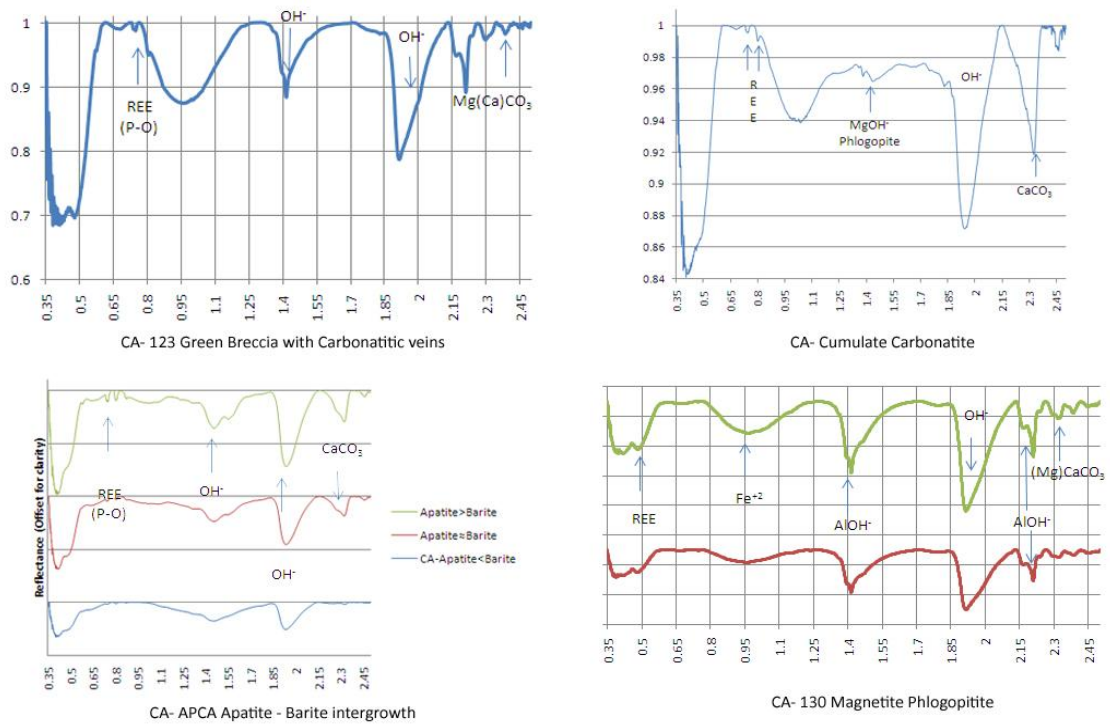


Figure 2 Reflectance spectra of phosphatic rocks from the Catalão I Carbonatitic Complex

XRF analyses confirm the sufficient presence of phosphates to be detected by reflectance and emissivity spectroscopy. For enough REE concentration, it was noted that CaO/P₂O₅ ratio had to be higher than 1,0, so that REE signatures show up in reflectance spectroscopy measurements. Although Ca takes part in the apatite structure, these results show that Ca can also mask the presence of phosphates in the SWIR region.

Table 2 X Ray Fluorescence for the studied samples

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I %	TOTAL
CA-103	1.2	0.9	0.0	15.8	0.18	0.8	43.5	0.07	0.02	35.7	0.4	98.6
CA-123	21.4	5.4	6.9	18.6	0.34	7.2	18.2	0.00	0.18	14.1	6.3	98.6
CA-130	21.0	1.0	10.2	7.8	0.28	7.5	24.5	0.00	0.26	19.5	6.9	98.9
TA-235	32.5	1.8	9.5	12.1	0.26	7.8	14.6	0.00	5.45	11.5	3.8	99.3
TA-236	6.8	54.5	1.7	11.2	0.17	1.9	7.9	0.00	0.64	7.8	3.4	96.0

In the Tapira samples (Figure 3), the same REE absorption features can be observed at 0,55 μm, 0,75 μm and 0,8μm. Phlogopite is more abundant in this complex, but it has less resolved features when compared with the Catalão I samples.

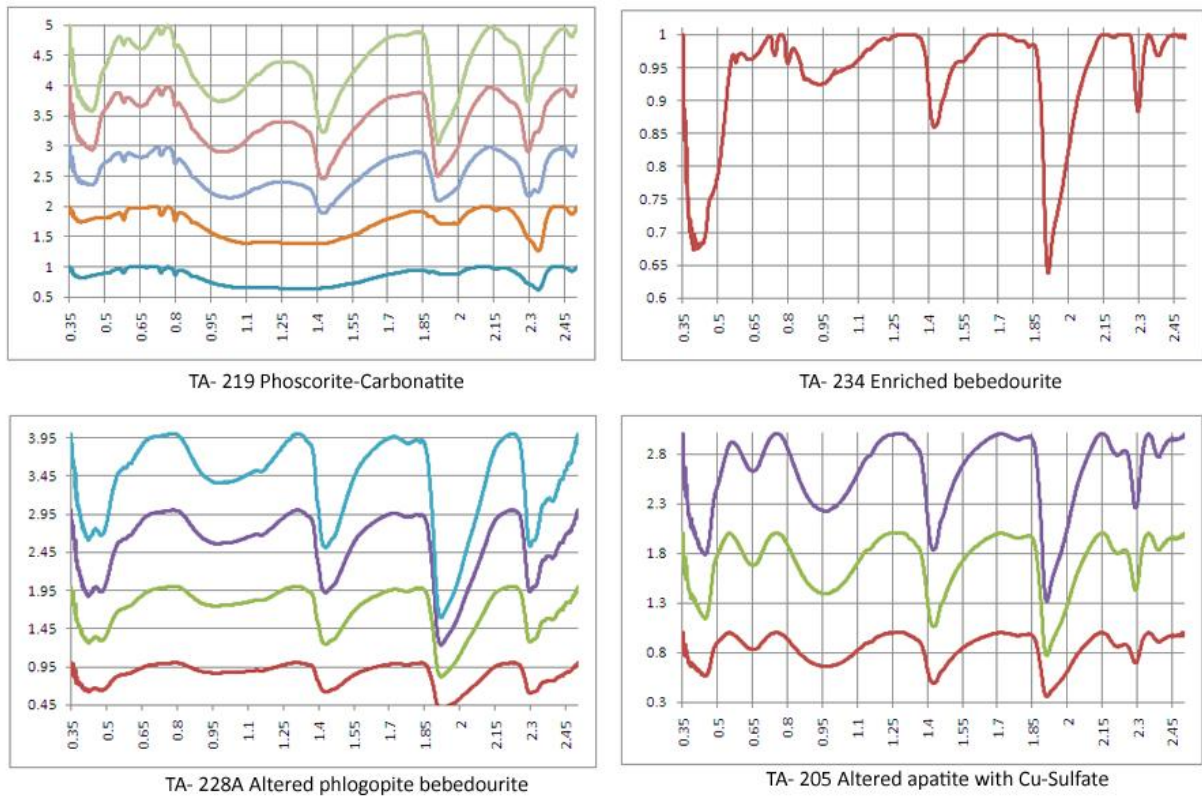


Figure 3 Reflectance spectra of phosphatic rocks from the Tapira Carbonatitic Complex

Emissivity spectra (Figure 4) display broad absorption features with doublets centered at $8,5\mu\text{m}$ related to the ν_3 fundamental vibration of P-O vibration bonds.

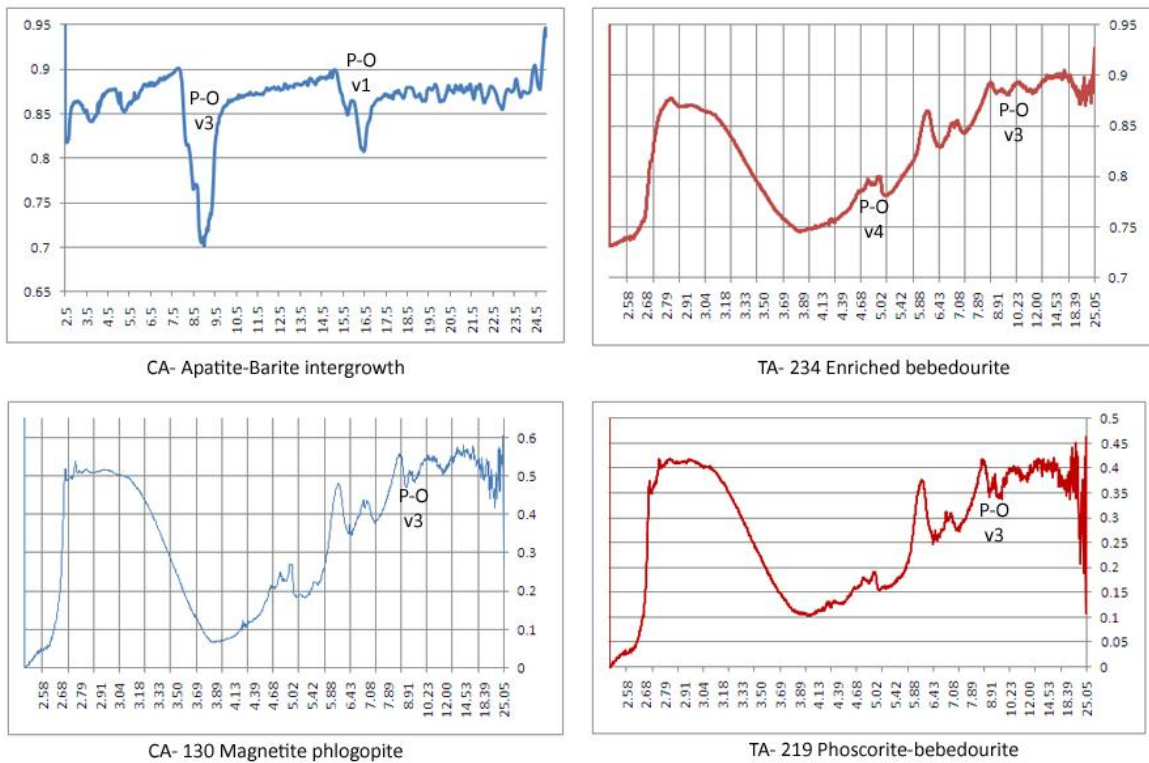


Figure 4 Emissivity spectra of phosphates from Catalão I and Tapira Carbonatitic Complexes.

5 Conclusions:

This work demonstrated that it is possible to identify several key minerals of a carbonatitic rock through reflectance and emission spectroscopy. Spectral signatures of Fe-Mg micas and variations in Fe-Mg-Ca carbonates can be used as mineralogical associations for the indirect detection of igneous phosphates through remote sensing data and techniques. These associations can be defined as:

- REE-Fe⁺³/Fe⁺²-for the VIS region of the spectra.
- Mg-mica (Phlogopite)-Calcite-dolomite-muscovite-kaolinite for the SWIR part of the spectra to find metassomatic phlogopites
- Calcite-ankerite-dolomite with associated SiO₂ for carbonatitic intrusions.

The fundamental ν_3 vibrations of phosphate minerals can be distinguished by several sensors, including orbital multispectral (ASTER) and airborne hyperspectral imagery. With this information is being prepared further research on the mapping of phosphatic rocks using ASTER images.

Petrological constraints to the mapping of phosphates are not sensitive to main sensors spectral record. From this, it should be possible to map phosphates that are associated with ferro-carbonatitic suites (ex. Iron Hill, Rowan *et al.*, 1986), calcium-carbonatites (Kaneshin, Mars and Rowan, 2011) and magnesium-carbonatites (Gem Park, Rowan *et al.* 1986).

XRD data show that even with alteration processes and degradation of the crystallization due to weathering (Tapira rocks are better preserved than those of Catalão I) it is possible to determine spectral features from altered soils and rocks of the Alto Paranaíba Igneous Province. The mineralogical associations of magnetite-fluorapatite; pyrochlore-anatase-fluorapatite and vermiculite-fluorapatite can be used as mineralogical endmembers on ASTER SWIR and TIR subsets as band ratios and relative band ratios, PCA analysis and sub-pixel classification methods (Matched Filtering, Mixture Tuned Matched Filtering).

Limitants to the associations are the exposure of altered soils and rocks as defined horizons by Oliveira & Imbernon (1998) and Toledo (1999). In this case, regional exploration still has to acknowledge the effect of vegetation cover to the prospection of phosphates.

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