

Mineralogical and Chemical Characterization of Vivianite Occurrence in Pegmatites from the Eastern Brazilian Pegmatite Province

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ABSTRACT

Vivianite samples were characterized by X-ray diffractometry and fluorescence analysis, ICP-OES and UV-VIS spectroscopy. The trace elements Ni, Co, Bi, Be, Ba, Li, Cr and Cu were detected. The experimental data suggest that high contents of Mn and Mg in substitution to Fe reduces the unit-cell parameters, and higher refractions indices and density can be related to the higher concentration of iron. The presence of Fe²⁺-Fe³⁺ intervalence charge transfer, spin-allowed d-d transitions of Fe²⁺ and octahedral Fe³⁺ is observed in the samples.

Keywords: Vivianite, pegmatite, Minas Gerais State, UV-VIS spectra, geochemical analyses, X-ray diffractometry.

INTRODUCTION

The Eastern Brazilian Pegmatite Province (EBPP) is spread over eastern Minas Gerais, western Espírito Santo, northern Rio de Janeiro, and southern Bahia states, and consists of a series of late to post-tectonic beryl-bearing and barren pegmatite bodies hosted in gneiss, schist, granite and quartzite within the Neoproterozoic Araçuaí Thrust-Fold Belt. This province is characterized not only by its geographic location but also by a particular geotectonic setting in a Neoproterozoic-Cambrian orogenic belt generated during the Brasiliano-Pan-African cycle, which consisted of a set of orogenies that lasted from about 850 to 550 Ma (Pinto & Pedrosa-Soares, 2001).

The Cigana Pegmatite, selected for this study is place in the Rio Doce valley in the Governador Valares and Galiléia regions, comprising rocks such as gneisses, a supracrustal schist sequence, sericite quartzite, and intrusive granitoids (Almeida, 1981; Cunningham *et al.*, 1996; Nalini *et al.*, 2000; Pedrosa-Soares and Wiedmann-Leonardos, 2000). The whole-rock age of the gneisses, determined by Rb–Sr, is 560 ±15 Ma, whereas K–Ar ages range from 525 to 670 Ma. Viana *et al.* (2003) distinguished two pegmatite generations in the northern portion of the EBPP. The older, 560 Ma pegmatites are related to the main stage of granitogenesis of the Brasiliano orogeny. They are more complex and evolved than the second pegmatite generation, which is dated at 500 Ma and related to the late stage of granitogenesis. The Galiléia intrusive granitic complex by U–Pb yield ages of 594±6 Ma (Nalini *et al.*, 2000). This work investigates the chemical and spectroscopic features of two vivianite samples, aiming to explain the formation of vivianite based on the paragenetic association and occurrence mode.

DESCRIPTION OF THE SAMPLES AND EXPERIMENTAL METHODS

The Cigana pegmatite is located in near to Galiléia region, and is a poorly zoned pegmatite body. A common feature of the pegmatite bodies from this region is the presence of phosphate minerals, and vivianite has been reported and investigated in this study. Mineralogically, this pegmatite is composed of quartz, muscovite, microcline, and albite as major

minerals, followed by more subordinate columbite, tryphylite, reddingite, hureaulite, fairfieldite, strunzite, rockbridgeite, pyrite, beryl and spodumene. Vivianite samples generally occur as well-developed prismatic and lamelliform grains with sizes ranging from 1 to 10 cm and striated parallel to the c-axis. The color is commonly light green to dark bluish-green with purple-green reflexes. The crystal of vivianite occur as open-space fillings fractures or in vugs in the Cigana pegmatite in paragenetic association with muscovite, albite, hureaulite, and pyrite. The samples were subjected to X-ray diffraction (XRD), X-ray fluorescence (ED-XFA), and ultraviolet and visible spectroscopy (UV-VIS), performed in the Analytical Techniques Laboratory – LAMUTA-ICET-UFMT, while analyses of inductively coupled plasma - optical emission spectrometry (ICP-OES) were performed in the Ambiental Geochemistry Laboratory – LGA-UFOP.

RESULTS AND DISCUSSION

The chemical composition, physical and optical properties are shown in table 1. There one can observe that higher refraction index and density are probably related with the increasing concentration of iron.

TABLE 1. Chemical analysis (oxides in % Wt and ions in ppm), structural, optical and physical properties of vivianite from Cigana Pegmatite.

	RC-V1	RC-V2		RC-V1	RC-V2
Fe ₂ O ₃	43.25 *	44.18 *	d	2.68	2.72
P ₂ O ₅	29.95 *	29.54 *	n _α	1.564	1.589
MnO	2.15 *	0.81 *	n _β	1.592	1.605
MgO	0.15 *	0.15 *	n _γ	1.630	1.641
CaO	0.10 **	nd	Birr	0.61	0.66
Al ₂ O ₃	0.17 *	0.14 *	a (Å)	10.048	10.023
SiO ₂	2.03 *	2.0 *	b (Å)	13.425	13.433
H ₂ O	22.26	23.05	c (Å)	4.675	4.685
Total	100.06	99.87	V (Å ³)	616.80	616.59
Ni	34 **	nd			
Co	<1 **	nd			
Be	3 **	nd			
Li	3 **	nd			
Cr	4 **	<300 *			
Cu	<1 **	<100 *			

Note: *: ED-XFA date; **: ICP-OES date; nd: not analyzed; H₂O = LOI

All loss on ignition content was assumed as being water content. The chemical analysis shows the existence of trace elements Ni, Co, Be, Li, Cr and Cu, therefore the sample composition is near the stoichiometric one. The

unit-cell parameters obtained using the main reflection lines of X-ray diffraction (Figure 1) range between 10.048 and 10.023 Å for *a*, 13.425 and 13.433 Å for *b* and 4.675 Å and 4.685 Å for *c*, with volume ranging from 616.80 to 616.59 Å³. All these values are lower than those of the ideal cell parameters, probably due to the presence of Mn²⁺ and Mg²⁺ ions substitutionally to Fe³⁺.

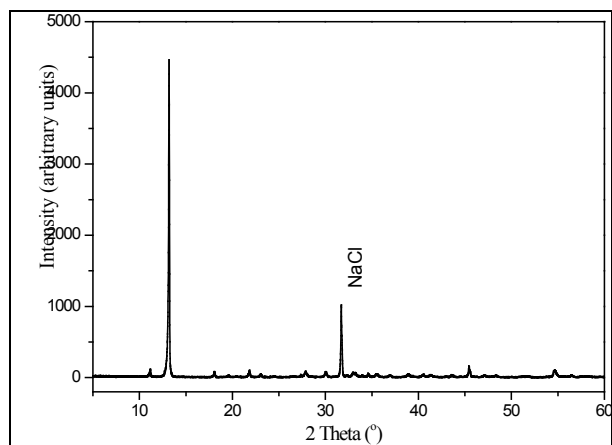


FIGURE 1. X-ray diffraction patterns (Cu-K_α radiation) of sample RC-V2 added NaCl.

The UV-VIS spectra (Figure 2) interpretations were given according to literature data (Faye 1968, Smith and Strens 1976, Smyth *et al.* 2005, Taran and Platonov 1998). The spectra were performed using unpolarized incident light parallel to the *b*-axis and are characterised by a large band at 870 nm and a shoulder at 680 nm, related to Fe²⁺-Fe³⁺ intervalence charge transfer, and a peak at 1020 nm associated to spin-allowed d-d transitions of Fe²⁺. The bands and shoulder between 340 to 600 nm were assigned to Fe³⁺ octahedral site.

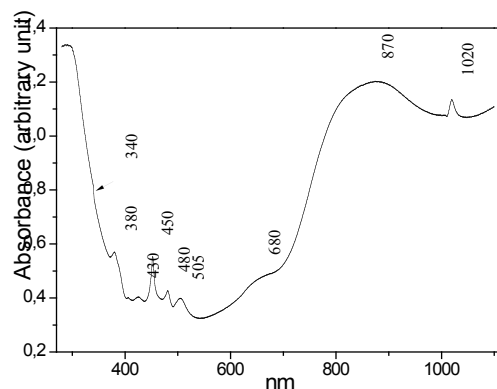


FIGURE 2. Unpolarized UV-VIS spectra of (010) cleavage sheet of vivianite with 0.03 mm thick.

Based on the geological setting, mode of occurrence and crystal sizes, vivianite formation may have taken place in the latest stages of the crystallization or in hydrothermal activity. The hydrothermal activity derived the metasomatism from primary to secondary phosphates and microcline to muscovite, beyond of the albitization process and transformation of phosphate masses into polycrystalline material. Cigana Pegmatite

can be classified petrogenetically as being of the LCT family, belong to rare element class because of the presence of beryl, columbite and some varieties of phosphates.

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