

## INOCENTE CAVE IN BRAZIL: X-RAYS DIFFRACTION AND SPECTROSCOPY OF MINERALS IDENTIFICATION

### CAVERNA DO INOCENTE, BRASIL: IDENTIFICAÇÃO DE MINERAIS POR DIFRAÇÃO DE RAIO-X E ESPECTROSCOPIA

Angelo Spoladore (1), João Paulo Trevisan Baú (2), Antonio Carlos Saraiva da Costa (3),  
Dimas Augusto Morozin Zaia (2) & Cristine Elizabeth Alvarenga Carneiro (2)

- (1) Departamento de Geociências-CCE, Universidade Estadual de Londrina, Londrina PR, Brazil.  
(2) Laboratório de Química Prebiótica, Departamento de Química CCE, Universidade Estadual de Londrina, Londrina PR, Brazil.  
(3) Departamento de Agronomia-CCA, Universidade Estadual de Maringá, Maringá PR, Brazil.

Contacts: [cristine@uel.br](mailto:cristine@uel.br).

#### Abstract

In the present work, the minerals from seven spots of Inocente cave, Tamarana city, Paraná state (Brazil), were collected and characterized using several techniques. Manganese minerals are found in all caves however each region concentrates minerals that depend on depositional environments (temperature, water, metals, organic matter and pH) and these factors have an effect on the structure and composition of the samples. The air inside the Inocente cave has an average temperature of 20°C and the water running through it has an average temperature of 18°C. The pH of the water inside the cave ranged from 5.2 to 7.0. Four minerals were identified in the Inocente cave: quartz, goethite, leucophosfite and todorokite. XRD showed that the goethite found in the Inocente cave has different degrees of crystallinity expressed due to their variable particles size. FT-IR also showed characteristics bands of goethite at 620, 797 and 892 cm<sup>-1</sup> belonging to Fe-O bond. Leucophosphite, an hydrous iron potassium phosphate was identified by XRD characteristics peaks and FT-IR characteristics bands at 985 and 1060 cm<sup>-1</sup> from P-O bond. Probably, leucophosphite was synthesized from the reaction between H<sub>3</sub>PO<sub>4</sub> derived from leached guano and iron hydroxides. The FTIR spectrum of todorokite showed characteristics bands belonging to Mn-O stretching bands at 440, 509, 577 and 773 cm<sup>-1</sup>. Todorokite was also identified by XRD. Quartz was identified by FT-IR spectroscopy and XRD. In the samples which presents quartz, goethite, leucofosfite and todorokite, EDX analysis confirmed the presence of Si, Fe, Fe and P and Mn, respectively. All samples showed a weight loss at 100 °C due to water hydration. However, todorokite showed a significant higher loss of hydration water (65%). SEM images showed morphologies characteristic of quartz, leucophosphite, todorokite and goethite.

**Key-Words:** caves, iron oxide-hydroxides, manganese oxides, quartz.

#### Resumo

No presente trabalho sete minerais coletados na caverna do Inocente, em Tamarana, Paraná (Brasil), foram caracterizados usando várias técnicas. Em toda extensão da caverna foi encontrado mineral de manganês no entanto cada região possui quantidades de depósitos de diferentes minerais, quais dependem do ambiente (temperatura, presença de água, metais, matéria orgânica e pH) e esses fatores mostraram ter efeito direto na estrutura e composição de cada amostra. A temperatura média da caverna foi de 20 °C e o rio de água corrente no interior da caverna apresentou uma temperatura de 18 °C. O pH da água ficou entre 5,2 a 7,0. Foram identificados quatro minerais: quartzo, goethita, leucofosfita e todorokita. Os difratogramas de raio-X mostraram que a goethita encontrada na caverna apresentaram uma variação na cristalinidade devido aos diferentes tamanhos de partículas, o FT-IR também mostrou bandas características da goethita em 620, 797 e 892 cm<sup>-1</sup> correspondendo ao grupo Fe-O. A Leucophosphita, um mineral de fosfato foi identificado por DRX e FT-IR com bandas características em 985 e 1060 cm<sup>-1</sup> devido ao grupo P-O. Provavelmente, leucophosphita foi sintetizada da reação entre H<sub>3</sub>PO<sub>4</sub> derivado da lixiviação de excrementos de morcego e hidróxidos de ferro O FTIR da todorokita mostrou bandas do grupo Mn-O, referente ao movimento de estiramento, em 440, 509, 577 e 773 cm<sup>-1</sup>. Todorokita foi também identificada por DRX. O Quartzo foi identificado por espectroscopia de FT-IR e DRX. A análise de EDX confirmaram a presença de Si, Fe, Fe e P e Mn nas amostras quais apresentaram os minerais quartzo, goethita, leucofosfita e todorokita, respectivamente. Todas as amostras apresentaram perda de massa a 100 °C devido a água de hidratação na análise térmica. Entretanto, a todorokita mostrou significante perda de massa (65 %). As imagens de

*microscopia eletrônica de varredura, SEM, mostraram as morfologias características dos minerais identificados, quartzo, leucophosfita, todorokita e goethita.*

**Palavras-Chave:** caverna, óxido-hidróxidos de ferro, óxido de manganês, quartzo.

## 1. INTRODUCTION

The interaction between minerals and organic components that make up the bulk of the sediments are relatively poorly understood. They can represent a potentially important source of information on the archaeology and site formation processes. Knowledge of organic and mineral interactions is relevant date for Brazil, since the country is under tropical climatic condition, therefore the changes which occur in organic materials are fast.

The chemistry, mineralogy and genetic aspects of the formation of minerals have been extensively studied in many caves (Moore, 1981; Khashima, 1983; Onac et al., 1997; Northup et al., 2003; Gázquez et al., 2011; Gázquez et al., 2012a; Gázquez et al., 2012b). Brazil has many caves with large variety of minerals, however few studies describe and characterize the assemblage of minerals. In Paraná state there are several caves developed in ornate sandstone, basalt and transition sandstone/basalt. In the state it is possible to see numerous outcrops of the Botucatu sandstone formation and the presence of caves. Inside these caves it can be seen different speleothems such as speleogems, cauliflowers and other forms such as corals, stalactites, stalagmites, curtains, cascades, columns, circles and others. The iron and manganese oxides and hydroxides speleothems are common in these caves (Spoladore & Cottas, 2007). In Tamarana region have sandstone/basalt soil and predominant caves are sandstone with ornaments of Fe and Mn content. The presences of these minerals (Fe and Mn) in caves reflect the soils composition. Martins (1985) proposed a classification of the quartz lithologies and defined the provinces and districts of caving. It should be pointed out that according to Spoladore & Cottas, 2007, this region received a specific rating as the division of sandstone speleological district due to physical discontinuity of the outcrops and the most obvious and striking tectonic with respect to the district of São Gerônimo da Serra. Saint Jerome da Serra.

Spoladore & Cottas (2007) identified the ornaments in several sandstone caves located in Tamarana, Paraná state (Brazil). In Tamarana, there is a distinct sandstone speleological area localized the Inocente cave. The mineralogy of ornaments, inside these natural areas, depends on the environmental conditions in the cave. The

speleothems composed of silica, calcite, and iron oxides are considered deposits of circulating water having its genesis related to dripping and oozing saturated aqueous solutions of these compounds. Fe and Mn oxide minerals are common minerals in the soils, sediments, and freshwater environments around the caves and might play a critical role in controlling the geochemical distribution of trace elements (Brown and Parks, 2001; Manceau et al., 2002). Fe and Mn oxides can be found, in cave and karst systems, as sedimentary fills, walls, ceilings, and floor coatings/crusts, and their own speleothems (Palmer, 2007).

In the present work, the minerals from seven spots of Inocente cave, Tamarana, Paraná state (Brazil), were characterized using several techniques such as FTIR spectroscopy, scanning electron microscopy (SEM), thermal analysis (TG, DTG), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). These analyses were used to discuss the formation of the minerals in the cave environment.

## 2. MATERIAL AND METHODS

### 2.1. Site description

Figure 1 shows the geographic location of Paraná State in Brazil, South America within the world map and Inocente cave sampling site. Inocente cave is located 70 km away from Londrina-PR in the county of Tamarana, northern state of Paraná, in 22k0486011 UTM coordinates 736 303 and at 814 m of altitude. The cave is located in a rural area occupied by agriculture and cattle raising. The original subtropical forest was cut and burned in the late 50's. Today the predominant vegetation are grasses species with a few forest fragments where native species still can be found. Inocente cave is located near the Botucatu sandstone formation in the boundary of basalt flood volcanism from the Trapp (jurassic-cretaceous). The Inocente cave is inserted in the geomorphological unit of the third Paraná plateau, in the transition area to the second plateau. Near the cavity dominates a relief of milder forms with rounded hills and convex profiles. Gaps also occur with sudden high slope (over 100% declivity). Valleys are observed in a "V" shape with open drains causing much embedded deep valleys and

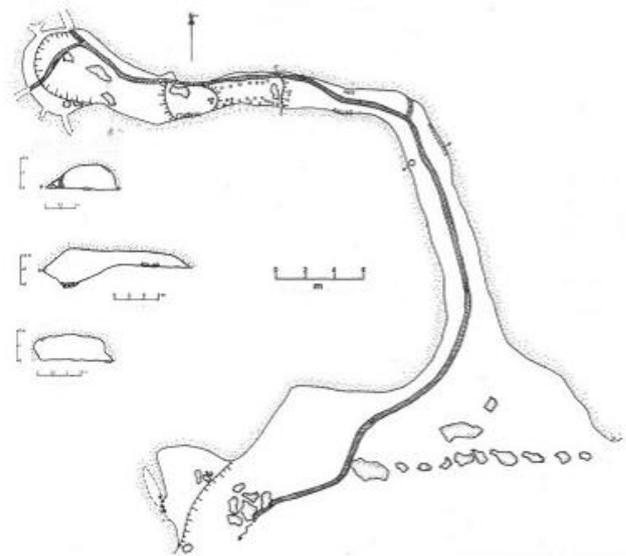
walls vertically integrated. The cave is in the River Plate basin. From the cave rises a small stream without a formal name, which is a direct tributary of the River Plate.

average height of one meter and an average width of two meters. The cave floor is covered by sandy sediments and soils, yielding, locally, some sedimentary deposits.



**Figure 1:** Location Inocente Cave. Spoladore and Cottas (2007).

The Inocente cave is 50 m long, basically a narrow corridor, without the formation of halls or other large spaces (Figure 2). Although the cave mouth is wide, its interior features the roof with an



**Figure 2.** Cartographic representation cave of the Innocent. Spoladore and Cottas (2007).

## 2.2. Field sampling

The rock materials (pebbles and cobbles) were collected at select locations along the cave. The rock pieces were removed from the cave and gently rinsed in the stream of the cave to remove adhered sediments and them placed in a sealable plastic bag. The seven samples collected were identified with letters (A, B,... and G) (Figure 3) and sent to the laboratory, dried at room temperature, grinded to < 0.53 mm for homogenization purposes.



**Figure 3:** Field sampling with the ornaments in Inocente cave. A, B, C, D, E, F G

### 2.3. pH and temperature determinations

The pHs were measured in situ along the cave, in the river and in the flowing waters. The air and water temperature inside the cave were measured in the winter and in the summer. The water temperature was  $18.0 \pm 0.3$  °C along the cave. The environment temperature was  $21.0 \pm 0.4$  °C in summer and  $18 \pm 0.2$  °C in winter.

### 2.4. X-ray diffraction

The grinded materials were analyzed by powder X-ray diffraction using a Shimadzu D 6000 diffractometer,  $\text{CuK}\alpha$  radiation (40 kV, 30 mA), a step-scanning mode ( $0.02^\circ 2\theta/0.6$  second) and 5 to  $70^\circ 2\theta$  amplitude. All peaks positions were analyzed using X'Pert HighScore 2.1 and the program Origin (8.0, 2007) software.

### 2.5. FTIR spectroscopy

The IR spectra were recorded with a Shimadzu FTIR 8300 spectrophotometer from 400 to  $4000\text{ cm}^{-1}$ , using pressed KBr disks with a resolution of  $4\text{ cm}^{-1}$ , after 95 scans. FTIR spectra were analyzed using the Origin program (8.0, 2007).

### 2.6. SEM

Scanning electron microscopy images were collected in Philips equipment produced by Quanta 200 (FEI) equipped with an energy dispersive X-ray (EDX) model INCA 200 at 30 keV from the Scanning Electron microscopy and Microanalysis laboratory facilities at UEL. The samples were fixed on 'stubs' using carbon adhesive tape, and then coated with a layer of gold.

### 2.7. Thermal analysis

Thermogravimetry (TG) and differential thermo-gravimetry (DTG) were conducted on TA Instruments TG analyzer (TGA, 4000 Perkin-Elmer). Nitrogen was used as purging gas and the flow rate was controlled at  $20\text{ mL min}^{-1}$ . For each run, 25 mg of each powder sample were loaded onto silicon pan and heated of  $30$  °C to  $780$  °C at heating rate of  $10$  °C  $\text{min}^{-1}$ .

## 3. RESULTS

### 3.1. Ornaments

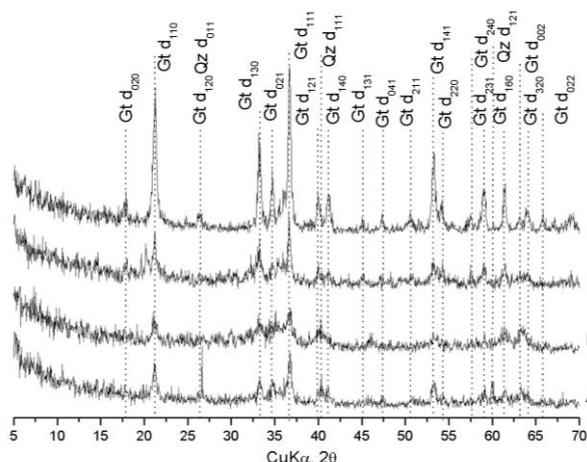
Figure 3 shows the field sampling site with some ornaments found in the cave. The ornaments were classified as suggested by Spoladore and Cottas (2007): stalactites and stalagmites, speleogems surfaces, silica and iron oxides crusts with concentric forms, and curtain with iron composition.

### 3.2. Energy-dispersive X-rays spectroscopy (EDX) analyses

Table 1 shows the elemental analyses of samples collected in the Inocente cave. The EDX results analyses of the A-G samples revealed iron, oxygen, silicon and phosphorus. Besides these elements, aluminum in the A, E, F and G and potassium in the C, E and F samples were also identified. Sulfur was found only in the C. Titanium and magnesium were identified only in the F sample. The G sample also showed occurrence of sodium and manganese.

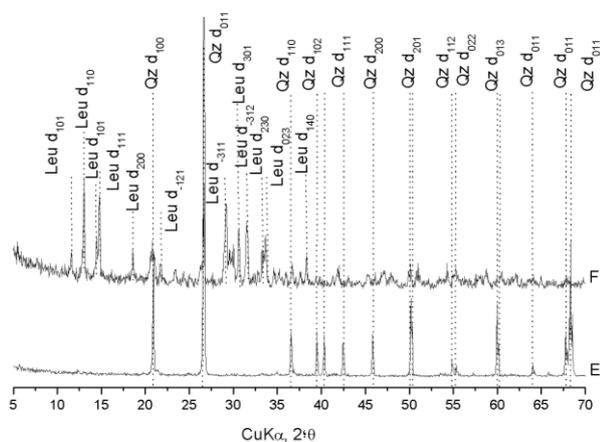
### 3.3. X-ray diffraction data

Figures 4-6 show X-ray diffractograms of the samples A-G collected inside the Inocente cave. Figure 4 shows the basal d-spacing of goethite as well as quartz peaks appear at  $26.6^\circ$ ,  $40.29^\circ$  and  $59.97^\circ 2\theta$  in the A sample. The peak  $d_{110}$  in the A, B and C samples showed a decrease in intensity and enlargement when compared with the sample D (Figure 4), which could be attributed to smaller degree of crystallinity of these materials.



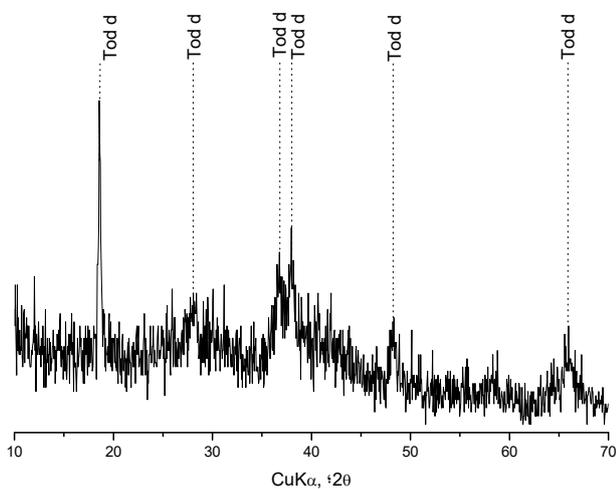
**Figure 4:** X-ray diffraction patterns for A, B, C and D samples of Inocente cave. The spots of collect are shown in the Figure 3. Qz = quartz, Gt = Goethite.

In the E and F diffractograms it was possible to identify the minerals quartz and leucophosphite (Figure 5). Quartz with high degree of crystallinity was also identified in the E sample by the sharp intense  $d_{100}$ ,  $d_{011}$  and  $d_{201}$  reflexes (Figure 5).



**Figure 5:** X-ray diffraction patterns for E and F samples showing the main reflections. The spots of collect are shown in the Figure 3. Qz = quartz, Leu = leucosfite.

The X-ray diffractogram of the G sample showed peaks with smaller intensity identified attributed to a manganese oxide (Todorokite) (Figure 6). It should be noted that the presence of manganese was confirmed by EDX (Table 1).



**Figure 6:** X-ray diffraction patterns for G sample showing the main reflections. The spot o collect is shown in the Figure 3. Tod = todorokite.

### 3.4. FTIR spectroscopy

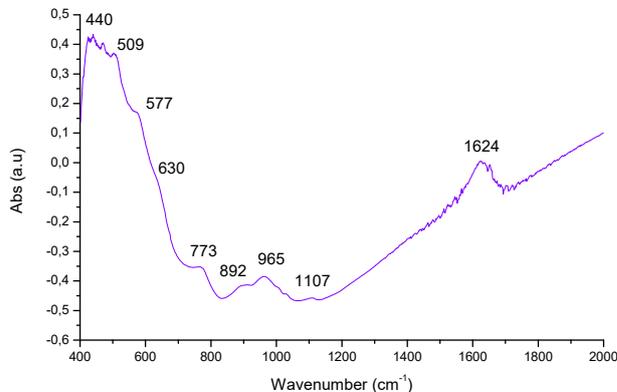
The FTIR spectrum of the G sample (Figure 7) showed the following bands 440, 509, 577 e 773  $\text{cm}^{-1}$  which could be attributed to Mn-O stretching and the band at 1624  $\text{cm}^{-1}$  to water O-H bending. (Feng, 1995; Cui et al., 2009).

FT-IR spectra of A-D samples are shown in Figure 8. The bands at 620, 797 e 892  $\text{cm}^{-1}$  belong to Fe-O bond, which are characteristic bands of goethite (Schwertmann et al., 1985; Cornell and Schwertmann, 2003). In sample C it was identified the P-O bands at 985 and 1060  $\text{cm}^{-1}$ , attributed to the presence of a phosphate group. For these samples (A-D) the FTIR spectra confirm the EDX results, which showed the presence of Fe, O and P (Table 1).

**Table 1.** EDX identification of atomic elements of A-G samples.

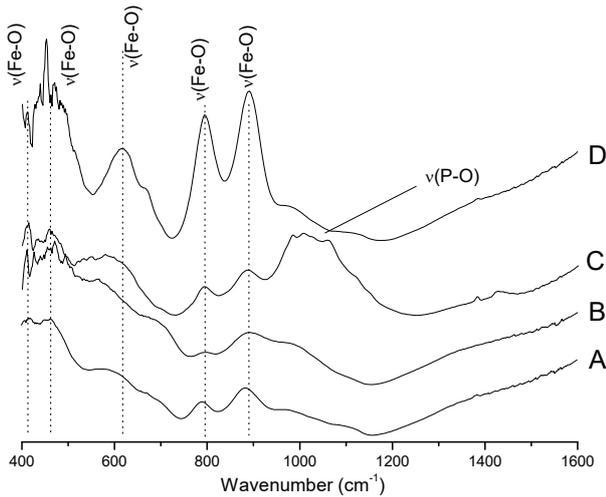
Element	A	B	C	D	E	F	G
Al	+	-	-	-	+	+	+
Co	-	-	+	-	-	-	-
Cu	-	-	-	-	-	-	+
Fe	+	+	+	+	+	+	+
Mn	-	-	-	-	-	-	+
K	-	-	+	-	+	+	-
Na	-	-	-	-	-	-	+
Mg	-	-	-	-	-	+	-
O	+	+	+	+	+	+	+
P	+	+	+	+	+	+	+
S	-	-	+	-	-	-	-
Si	+	+	+	+	+	+	+
Ti	-	-	-	-	-	+	-

(+) = The element was identified in the sample.  
(-) = The element was not identified in the sample.  
The spots o collect are shown in the Figure 3.



**Figure 7:** FT-IR spectrum of the G sample. The spot of collect is shown in the Figure 3.

Figure 9 shows the FT-IR spectra of the E and F samples, these spectra supplied characteristics bands of Si-O, Fe-O and P-O groups. The FT-IR spectrum of the E sample shows characteristic band of Si-O that could belong to quartz. The FT-IR spectrum of the F sample shows characteristic bands due to P-O bonds, which belong to the phosphate mineral, leucophosphite. The presence of these elements is in agreements with EDX results (Table 1).

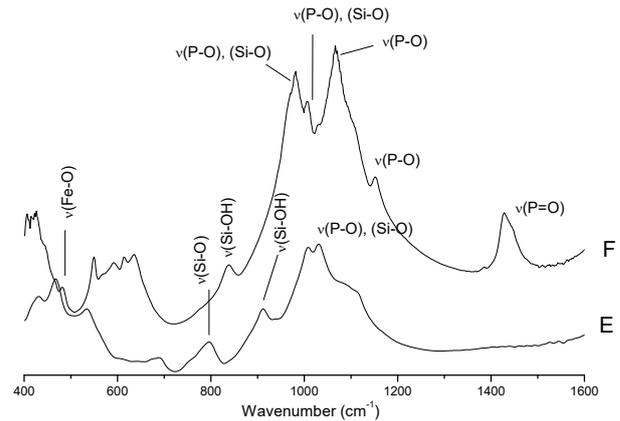


**Figure 8:** FT-IR spectra of A, B, C and D samples showing the main groups. The spots o collect are shown in the Figure 3.

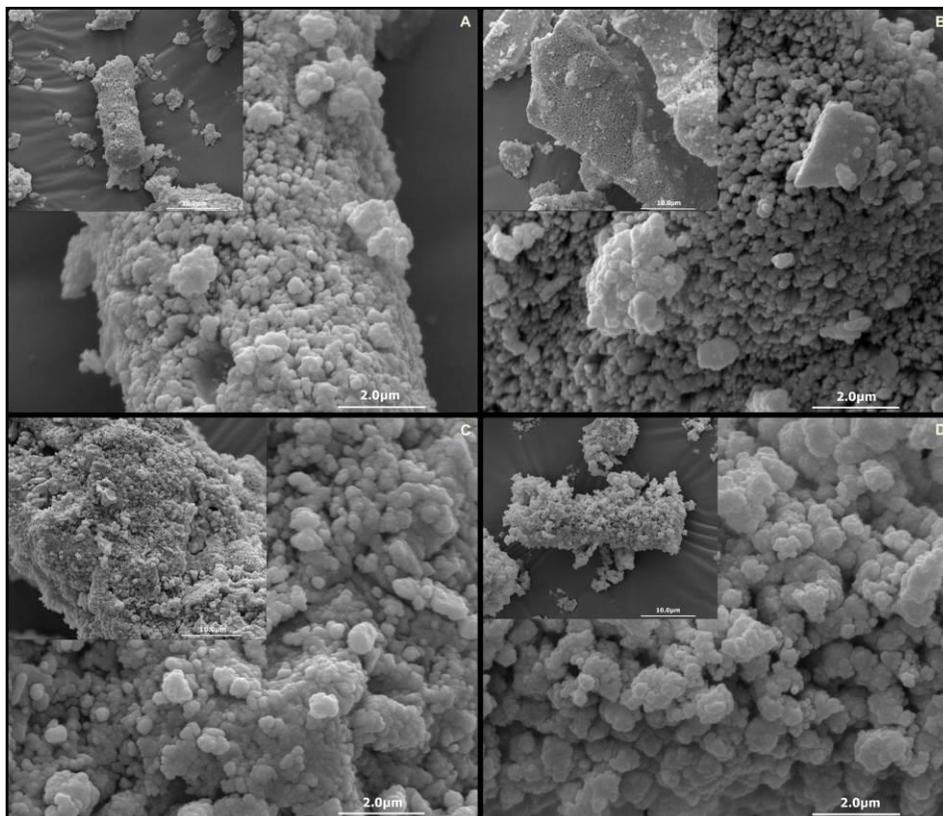
### 3.5. SEM

Figures 10-12 illustrate the SEM images of A-G samples. The SEM images in the figure 10 (A-D samples) showed morphology of goethite crystals, which were confirmed by FT-IR spectroscopy (Figure 8) and X-ray diffractometry (Figure 4). All samples in figure 10 have hexagonal and spherical aggregates morphology. The B sample has an ordering in the arrangement of particles and none of the images showed an acicular particle, which would be the common morphology and indication of fine

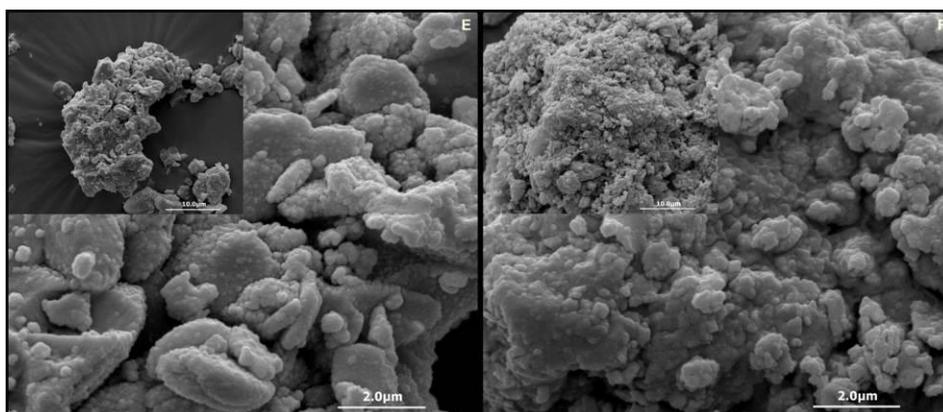
crystalline materials. Figure 11 shows SEM images of E and F samples which morphology belong to a mixture of quartz and leucophosphite, respectively. These results were confirmed by X-ray diffractometry (Figure 5) and FT-IR spectroscopy (Figure 9). The natural material has hexagonal and spherical aggregates with some irregular particles which are cemented on the surface of quartz grains. The SEM images of G sample showed morphology with shapes that resemble stacked plates or lamellae, found in similar deposits in caves (Figure 12) (Friedrich et al., 2011).



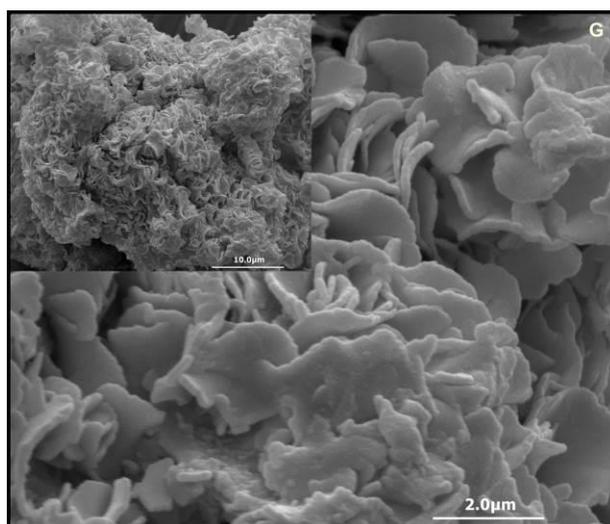
**Figure 9:** FT-IR spectra of E and F samples showing the main groups. The spots of collect are shown in the Figure 3.



**Figure 10:** SEM images of A and D samples. The spots o collect are shown in the Figure 3.



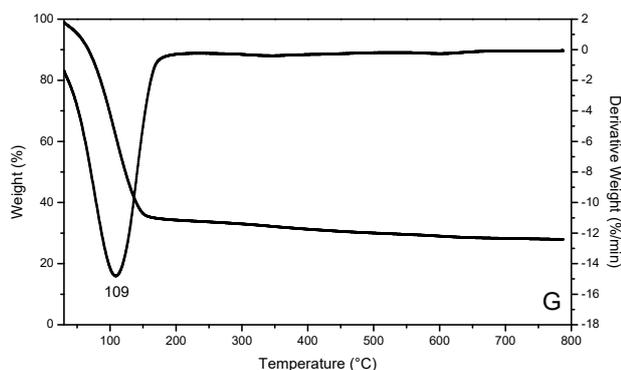
**Figure 11:** SEM images of E and F samples. The spots of collect are shown in the Figure 3.



**Figure 12:** SEM images of G sample. The spot of collect is shown in the Figure 3.

### 3.6. Thermal analysis

Figures 13-15 illustrate TG and DTG curves of A-G samples. For all samples the weight loss up to 100 °C indicates water hydration (Figure 13-15). Sample G has significant amount of water hydration, about 65 % (Figure 13). For the E and F samples (Figures 15), TG and DTG curves provided events below 200 °C, that were interpret as water hydration weight loss. The events above 200 °C were attributed to the loss of structural water in the minerals (Figure 15).



**Figure 13:** TG curve and DTG of G sample. The spot of collect is shown in the Figure 3.

## 4. DISCUSSION

Iron and manganese oxides were found in all cave extension. On the floor and under the roof of the Inocente cave is possible to observe rounded forms indicating that water was an important factor to the cave development. This cave is located in Silver River watershed (Spoladore and Cottas, 2007). The floor is covered by sandstone sediments originated from sedimentary deposits. The entrance of Inocente cave is covered by sandy sediments, in the middle by large amount of iron and manganese deposits, and at the end there is a small hall whose predominance is iron oxides. Only iron oxides precipitation is apparently shown in the roof of these localities. Friedrich et al. (2011) found the same characteristic in Southwestern Illinois karst with the iron oxides and manganese deposits along the cave. According to Friedrich et al. (2012), there were two depositional environments in cave, one with Fe and Mn precipitations were due to anoxic groundwater that enters into the cave and the other one was due to direct deposition from the cave stream.

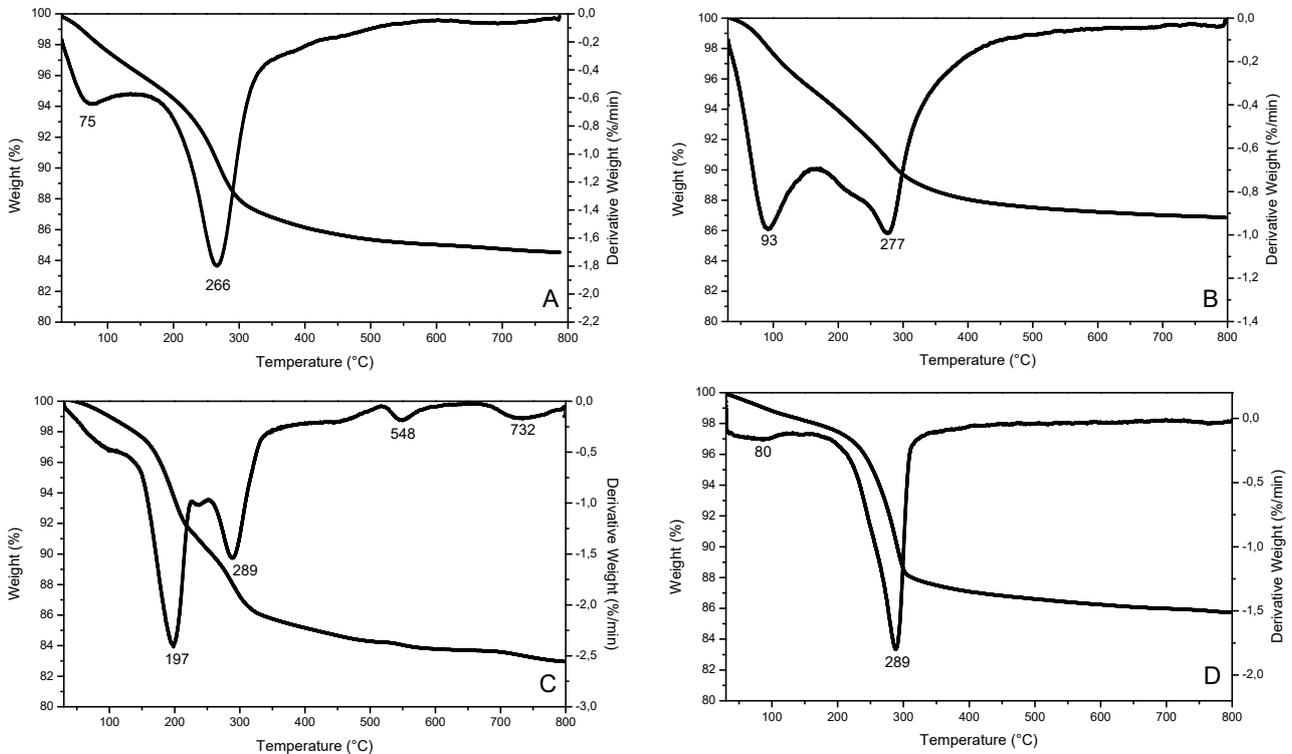
The predominance of goethite in Inocente cave was evidenced in A-D samples by XRD results (Figure 4) and also showed several degrees of crystallinity and particles sizes. The particles sizes are influenced by temperature of the precipitation, that inside the cave is about 20°C and the water is about 18°C. Schwertmann et al. (1985) showed that the goethite properties are affected by temperature of synthesis, which in the range from 4 to 90°C, the crystals size increases with the temperature. The evidence and predominance of goethite, in great part of Innocent cave, comes from its hydrogeochemistry process. The region where Inocente cave is located has sandstone and basalt rock outcrops. The sandstone is intercalated with claystones, siltstones, other sandstones and pebble conglomerates (concretions) of clays (Spoladore and Cottas, 2007).

Besides the temperature, the size of goethite particles also depends on the water pH. Hernandez et

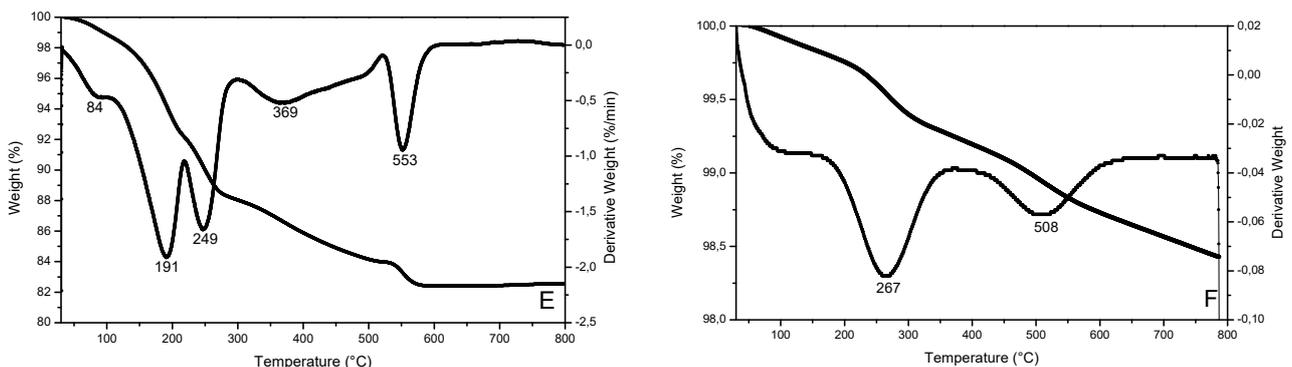
al. (2011) studied goethite formation in laboratory, from pH 2.5 to 13.5. In the first stage, the authors associated with the formation of ferric hydroxide gel, under acid conditions; the second have spontaneous nucleation of goethite from gel, under alkaline conditions and the first sedimentable particles; and third the growth of goethite in alkaline conditions that have the acicular form. In the natural system, the formation of goethite is similar to laboratory conditions and are associated with the dissolution of quartz.

Quartz is an important mineral constituent in sandstone cave and can be seen in sample E (Figure 5). The quartz dissolution in water is a simple hydration process (Aubrecht et al., 2011). The formation of silicic acid increases the quartz solubility which raises the pH to 9.0. This basic

environment favors goethite formation by  $Fe^{3+}$  precipitation, which has its origin in basaltic soil formation in region. The pH was measured in some regions in the Inocente cave and ranged from 5.2 to 7.0. Because the low pH of Inocente cave, goethite nucleation occurred but the size of the particles is small. This can be observed by the SEM images, which showed spherical but no acicular particles (Figure 10). The pH associated with temperature of Inocente cave probably affect the particle growth that in this case is a slow process. The fragmentation and frayed appearance of the filaments and fibrils in iron oxides are due to aging of the material, possibly undergoing a recrystallization process (Chan et al., 2009; Frierdich et al., 2011). A variety of colors are observed to goethite materials, that have yellow to red hues, but the predominance is yellow color.



**Figure 14:** TG curves and DTG of A - D samples. The spots of collect are shown in the Figure 3.



**Figure 15:** TG curves and DTG of E and F samples. The spots o collect are shown in the Figure 3.

FTIR spectra of the A-D samples showed bands belonging to Fe-O group and in the C sample the band belong to P-O group was also observed (Figure 8). The FT-IR spectra also showed that crystallinity of goethites was low when compared to the same synthetic materials described by Carneiro et al. (2013). These results were also confirmed the XRD (Figure 4). Many caves are formed by direct deposition of materials that composes the water streams that flow into the caves, and this type of deposition is found in the caves around the world, the difference among the depositions are due to the time spent for the precipitation and the chemical environment in the caves (Friedrich, et al.2011).

For the A-D samples the larger weight losses occurred in the temperature range from 75 to 289°C (Figure 14), these losses could be attributed to water onto the surface and into the structure of the samples. For the C sample the weight loss, in minor portion, also occurs in 548°C and 732 °C (Figure 14). The transformation phase of quartz initiate in 500°C and the total transformation occurs about 700°C. For A-D sample, the weight loss was about 12-15% (Figure 14).

The XRD of the F sample showed leucophosphate mineral (Figure 5), that are usually found in caves when organic material mainly due to bat excrements are present (Branco and Chaves, 2006). The phosphate is derived mainly from organic material that breaks down due to oxidation. Thus, leucophosphate forms through the reaction between H<sub>3</sub>PO<sub>4</sub> derived from leached guano and iron hydroxides. The leucophosphate mineral is associated with goethite since the iron can form a complex with phosphorus in inner sphere bond. Leucophosphate [K(Fe<sup>3+</sup>)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)·2H<sub>2</sub>O] is a phosphate mineral that crystallize in the monoclinic system. According to Giurgiu and Tămaş (2013), phosphate minerals can provide information about the environment in which they have been synthesized. It should be noted that leucophosphate is formed in acidic environment.

## REFERENCES

- AUBRECHT, R., LÁNCZOS, T., GREGOR, M., SCHLÖGL, J., ŠMÍDA, B., LIŠČÁK, P., BREWER-CARIÁS, CH., VLČEK, L. Sandstone caves on Venezuelan tepuis: Return to pseudokarst? *Geomorphology* 132, 351–365, 2011.
- BASKAR, S., BASKAR, R., LEE, N., KAUSHIK, A., THEOPHILUS, P.K. Precipitation of iron in microbial mats of the spring waters of Borra Caves, Vishakapatnam, India: some geomicrobiological aspects. *Environ. Geol.* 56, 237–243,2008.

XRD and FT-IR spectroscopy confirmed the presence of Todorokite in the Innocent cave (Figures 6 and 7). Feng (1995), Cui et al. (2009) and White et al. (2009) showed that the bands at 440, 509, 577 and 773 cm<sup>-1</sup> could be attributed to Mn-O stretching. The band at 1624 cm<sup>-1</sup> could be attributed to OH due to hydration of water molecule (Feng, 1995).The occurrence of this mineral in nature is common and arises from their similar chemical properties and biological activity (Miller et al., 2012). Mn oxides can be found in cave as sedimentary fills, as wall, ceiling, and floor coatings/crusts (Palmer, 2007). SEM images showed that Todorokite has a good crystallinity (Figure 12). For this mineral, the weight loss in TG analysis is associated to water in mineral surface (Figure 13).

## 5. CONCLUSION

This study has identified and described the minerals found in the Innocent cave. The minerals are found in all caves, however each region concentrates minerals that depend on different depositional environments and these factors have an effect on the structure and the composition of the samples. Fe oxy-hydroxides are found where groundwater enters the cave through the walls and through cracks in the ceiling with variable degree of crystallinity. In contrast, Mn oxides are deposited in mid cave with good crystallinity. In the Inocente cave it was also identified quartz, goethite, leucofosfite and todorokite.

## ACKNOWLEDGEMENTS

J.P.T.B. acknowledges the fellowship from Capes. This research was supported by grants from CNPq (no. 473076/2004) and Fundação Araucária (no. 2421). The authors are also grateful to Dr Célia G. T. de Jesus Andrade and Mr Osvaldo Capello from Laboratório de Microscopia e Microanálise for the MEV images and EDX analysis.

- BRANCO, P.M., CHAVES, M.L.S.C. A Mineralogia e alguns de seus minerais raros ou de gênese exótica. **Terra e Didática**. 2, 75-85, 2006.
- BROWN JR., G.E., PARKS, G.A. Sorption of trace elements on mineral surfaces: modern perspectives from spectroscopic studies, and comments on sorption in the marine environment. **Int. Geol. Rev.** 43, 963–1073, 2001.
- CARNEIRO, C.E.A., SOUZA, C.M.D., ZAIA, C.T.B.V, DE SANTANA, H., PAESANO JR., A., DI MAURO E, DA COSTA, A.C.S., SOUZA JUNIOR, I.G., IVASHITA, F.F., ZAIA, D.A.M. Synthesis of goethite in solutions of artificial seawater and amino acids: a prebiotic chemistry study. **Int. J. Astrobiol.** 12, 149-160, 2013.
- CHAN, C.S., FAKRA, S.C., EDWARDS, D.C., EMERSON, D., BANFIELD, J.F. Iron oxyhydroxide mineralization on microbial extracellular polysaccharides. **Geochim. Cosmochim. Acta** 73, 3807–3818, 2009.
- CORNELL RM, SCHWERTMANN U. **The iron oxides: structure, properties, reactions, occurrences and uses**. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003.
- CUI, H., FENG, X., TAN, W., HE, J., HUA, R., LIU, F. Synthesis of todorokite-type manganese oxide from Cu-buserite by controlling the pH at atmospheric pressure. **Microp. Mesop. Mat.** 117, 41–47, 2009.
- FENG, Q. Metal íon Extraction/Insertion reactions with Todorokite-Type Manganese Oxide in aqueous phase. **Chem Mater.** 7, 1722-1727, 1995.
- FRIERDICH, A.J., HASENMUELLER, E.A., CATALANO, J.G. Composition and structure of nanocrystalline Fe and Mn oxide cave deposits: Implications for trace element mobility in karst systems. **Chem. Geology** 284, 82–96, 2011.
- FRIERDICH, A.J., CATALANO, J.G. Distribution and speciation of trace elements in iron and manganese oxide cave deposits. **Geochim. Cosmochim. Acta.** 91, 240–253, 2012.
- GÁZQUEZ, F., CALAFORRA, J.M., FORTI, P., RULL, F., MARTÍNEZ-FRÍAS, J. Gypsum-carbonate speleothems from Cueva de las Espadas (Naica mine, Mexico): mineralogy and palaeohydrogeological implications. **Int. J. Speleology** 41, 211–220, 2012a
- GÁZQUEZ, F. CALAFORRA, J. RULL, F., Boxwork and ferromanganese coatings in hypogenic caves: An example from Sima de la Higuera Cave (Murcia, SE Spain). **Geomorphology** 177–178, 158–166., 2012b.
- GÁZQUEZ, F., CALAFORRA, J.M., FORTI, P. Black Mn-Fe crusts as markers of abrupt palaeoenvironmental changes in El Soplao Cave (Cantabria, Spain). **Int. J. Speleology** 40, 163–169, 2011.
- GIURGIU, A., TĂMAȘ, T. Mineralogical data on bat guano deposits from three Romanian caves. **Studia UBB Geologia** 58, 13–18, 2013.
- HERNANDEZ, G. M., BECK, P., RENARD, F., QUIRICO, E., LANSON, B., CHIRIAC, R., FINDLING, N. Fast Precipitation of Acicular Goethite from Ferric Hydroxide Gel under Moderate Temperature (30 and 70 C), **Crystal Growth & Design**, 11, 2264–2272, 2011.
- KHASHIMA, N., On the Wad-minerals from the cavern environment. **Int. J. Speleology** 13, 67–72, 1983.

- MANCEAU, A., MARCUS, M.A., TAMURA, N. Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques. In: Fenter, P.A., Rivers, M.L., Sturchio, N.C., Sutton, S.R. (Eds.), *Applications of Synchrotron Radiation in Low- Temperature Geochemistry and Environmental Science*. Washington D. C, **Mineralogical Society of America and Geochemical Society**, 341–428. 2002.
- MARTINS, S.B.M.P., **Levantamento dos Recursos Naturais do Distrito Espeleológico Arenítico de Altinópolis-SP**, Relatório Final, FAPESP, p. 121 protocolo 83/2552-3, São Paulo, 1985.
- MILLER, A.Z., DIONÍSIO, A., BRAGA, S.M.A., HERNÁNDEZ-MARINÉ, M., AFONSO, M.J., MURALHA, V.S.F., HERRERA, L.K., RAABE, J., FERNANDEZ-CORTES, A., CUEZVA, S., HERMOSIN, B., SANCHEZ-MORAL, S., CHAMINÉ, H., SAIZ-JIMENEZ, C. Biogenic Mn oxide minerals coating in a subsurface granite environment. **Chem. Geol.** 322–323, 181-191, 2012.
- MOORE, G.W.. **Origin of Black Deposits in Caves. Proceedings 8th International Congress of Speleology, Bowling Green I and II**, pp. 642–644, 1981.
- NORTHUP, D.E., BARNS, S.M., YU, L.E., SPILDE, M.N., SCHELBLE, R.T., DANO, K.E., CROSSEY, L.J., CONNOLLY, C.A., BOSTON, J., DAHM, C.N. Diverse microbial communities inhabiting ferromanganese deposits in Lechuguilla and Spider Caves. **Environm. Microbiol.** 5, 1071–108, 2003.
- ONAC, B.P., PEDERSEN, R.B., TYSSELAND, M. Presence of rare-earth elements in black ferromanganese coating from Vântuliu cave (Romania). **J. Cave Karst Studies** 59, 128–131, 1997.
- PALMER, A.N., **Cave Geology**. Cave Books, Dayton. 454 pp., 2007.
- SCHWERTMANN, U., CAMBIER, P., MURAD, E., Properties of goethites of varying crystallinity. **Clays Clay Min.**, 33, 5, 369-378, 1985.
- SPOLODORE, A. AND COTTAS, L. R., A Gruta do Inocente. **Informativo SBE**, 93, 24-27, 2007.
- WHITE, W.B., VITO, C., SCHEETZ, B.E. The mineralogy and trace element chemistry of black manganese oxide deposits from caves. **J. Cave and Karst Studies** 71, 136–143, 2009.

---

**Fluxo editorial:**

Recebido em: 21.05.2015

Aprovado em: 26.08.2015



A revista *Espeleo-Tema* é uma publicação da Sociedade Brasileira de Espeleologia (SBE).  
Para submissão de artigos ou consulta aos já publicados visite:

[www.cavernas.org.br/espeleo-tema.asp](http://www.cavernas.org.br/espeleo-tema.asp)