USE OF INFRARED SPECTROSCOPY ANALYSIS TO FOSSIL STRUCTURES OF BAURU BASIN, BRAZIL

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ABSTRACT – Analysis by infrared were carried out on powdered extracts of fossil elements like bones, eggshells and coprolites associated with crocodyliphorms. The material were collected from outcrops of Adamantina Formation of Upper Cretaceous Bauru Basin at General Salgado and Marília, State of São Paulo. The reference spectra used in the analytic procedures were those of powdered apatite, of synthetic salts of calcium carbonate and phosphate carbonate, and of fresh eggshells and excrements produced by current crocodylians, besides that of the host matrix in which the fossils occur. The analysis reveled that the fossil bones fragments and coprolites have strong similarity with calcium phosphate and apatite spectra, while the spectra of fossil eggshells and recent eggshells of modern crocodilian reveled strong similarity with calcium carbonate. The results from infrared analyses reveal that the technique is appropriate for the determination of fossilized bodies, with good precision and reliability.
Keywords: Infrared spectroscopy, paleochemistry, ichnofossils, Cretaceous.

RESUMO – *P.R. de F. Souto – Uso de análise por espectroscopia de infravermelho em estruturas fósseis da Bacia Bauru, Brasil.* Este estudo, analisa através da técnica de infravermelho extratos de ossos, cascas de ovos e excrementos fossilizados, pertencentes a crocodyliformes da Formação Adamantina, do Cretáceo Superior da Bacia Bauru. Esses materiais foram coletados em afloramentos localizados nos municípios de General Salgado e Marília, no Estado de São Paulo. Nos procedimentos de analise foram utilizados como espectros padrões extratos de apatita, de carbonato de cálcio e fosfato de cálcio e pulverizados frescos de cascas de ovos e excrementos produzidos por crocodilianos atuais, além da matriz sedimentar associada aos elementos fósseis. Os espectros obtidos revelaram que os fragmentos de ossos fossilizados e os coprólitos apresentaram grande afinidade com os espectros referentes ao mineral apatita e fosfato de cálcio, enquanto os espectros das cascas de ovos fossilizadas e recentes apresentaram forte similaridade com carbonato de cálcio. Os resultados das análises por infravermelho revelam ser uma técnica adequada na determinação de corpos fossilizados com boa precisão e confiabilidade.
Palavras-chave: Infravermelho, paleoquímica, ichnofosseis, Cretáceo.

INTRODUCTION

Infrared spectroscopy is known since about fifty years as an useful technique in the study of molecular structure of different industrial products like food and plastics. The highest selectivity of infrared spectroscopy has been used more recently in microbiology (Naumann & Labischinski, 1991), medicine (Daudon & Jungers, 1993) and fossils (Hallgren, 1987) for identifying biochemical components (Mantsch & McElhanet, 1990).

An infrared spectrum occurs because each functional group in a molecule has a consistent frequency at which it absorbs radiation. The intensity of the absorption is directly related to concentration; that is, as the concentration increases the absorption increases and the transmission decreases. The relative intensity of the absorption bands provides information about the concentration of the components in an unknown sample (Hill & Rendell, 1975).

The application of infrared spectroscopy is unlikely to displace the conventional fluorescence or microprobe methods already well established for determination of physical state of the organic and inorganic compounds like found in fossil structures. However, it provides a qualitative identification and quantitative analysis, uses small amounts of material and avoid to damage or destruction of specimens.

The infrared spectra of coprolites, eggshells and fossil bones, and dried modern crocodile excrements and eggshells are here analyzed and compared. All fossil elements were collected in General Salgado and Marília, State of São Paulo, in outcrops of Adamantina Formation, deposited during Upper Cretaceous in the Bauru Basin (Figure 1).

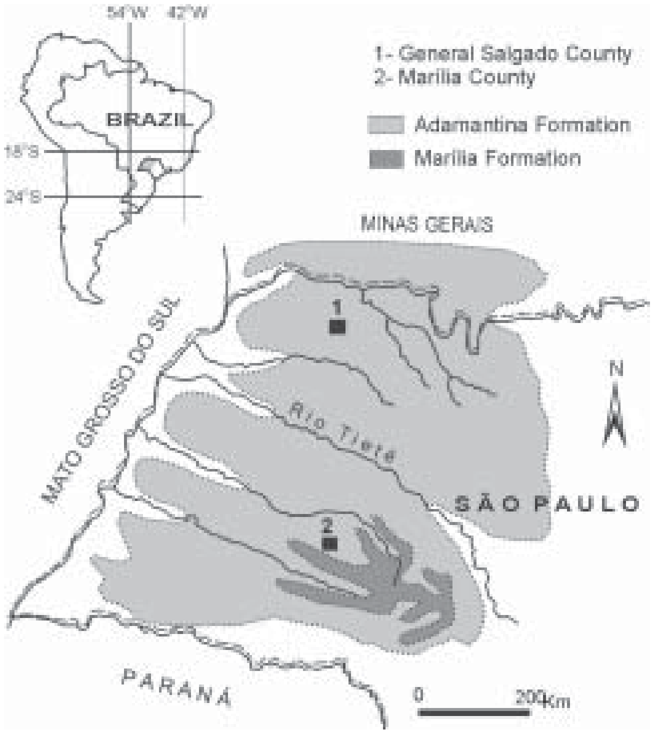

FIGURE 1. Location map.

MATERIAL AND METHODS

The infrared analysis were carried out in a Nicolet-Magna-IR 760 equipment of the Instituto de Química Inorgânica, Universidade Federal do Rio de Janeiro.

In the analysis the chosen references spectra were those of salts of calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$) e calcium phosphate ($Ca_2P_2O_3$) produced by Specpure (England) and Merck (Brazil), and of powdered extract of apatite.

The coprolites (UFRJ-DG 129-IcV and UFRJ-DG 350-IcV), eggshells (UFRJ-DG 298-IcV and UFRJ-DG 381 IcV) and bone fragments (UFRJ-DG 107-R and UFRJ-DG 286-R) analyzed are deposited in the collection of the Departamento de Geologia, Instituto de Geociências, Universidade Federal do Rio de Janeiro. The fresh excrements and eggshells were collected with collaboration of the Jardim Zoológico of Rio de Janeiro.

The samples were processed for analysis by separating 50 to 100 mg from the material. The powdered matrix-coprolites and sediment are detached by drill of 30 mm and 20 mm (Hirsch, 1979).

After grinding, 1 mg of each sample is added to 99 mg of KBr (1% solution) to create an uniform mixture, which is formed into a clear pellet using a die in a hydraulic press. The function of the KBr is to suspend the sample for the radiation beam and to reduce light scattering. The KBr pellet containing the sample is placed into the same holder of a detector TGS KBr, with mirror velocity of 0.6329, resolution of 4.000 and aperture of 90.000.

The fresh excrements and eggshells produced by modern crocodilian (*Caiman latirostris*) were processed through being dried for 6 hours at 100^{o}C and grinding by manual process until obtain an uniform and fine mixture (Souto, 2003).

The interpretation of a spectrum is based on the knowledge of where specific functional groups absorb that are derived from spectra of pure materials. These reference spectra provide the baseline data from which the interpretation of unknowns is made.

Whenever matrix was still attached or available, the infrared spectra were also processed in order to determine if the adjacent matrix influenced the fossils spectra. The samples were selected from different localities, General Salgado and Marília, from the same stratigraphic unit (Souto at al., 2005).

RESULTS

The functional group assignments are based on the spectra of pure compounds obtained in this study and consulting the Commercial Spectra List (Sadtler, 1959). The absorption at 1,480 to 1,420, 880 to 885 and

712 cm^{-1} correspond to calcium carbonate, the absorption bands at 1,090, 1,033, 600, and 570 cm^{-1} is due to calcium phosphate and apatite; water absorbed during sample preparation is at 3,600 to 3,000 cm^{-1}, and the absorption bands at 2,850 to 2,900 is due of the organic material. The data also shows that the spectrum of the magnesium carbonate has a unique absorption bands in 1,120 and 594 cm^{-1} (Figures 2, 3, 4 and 5).

The first results reveal absorption bands of magnesium carbonate only in fossil bone fragments, and any trace of this compound was detected in the coprolites and the eggshells (Figure 6).

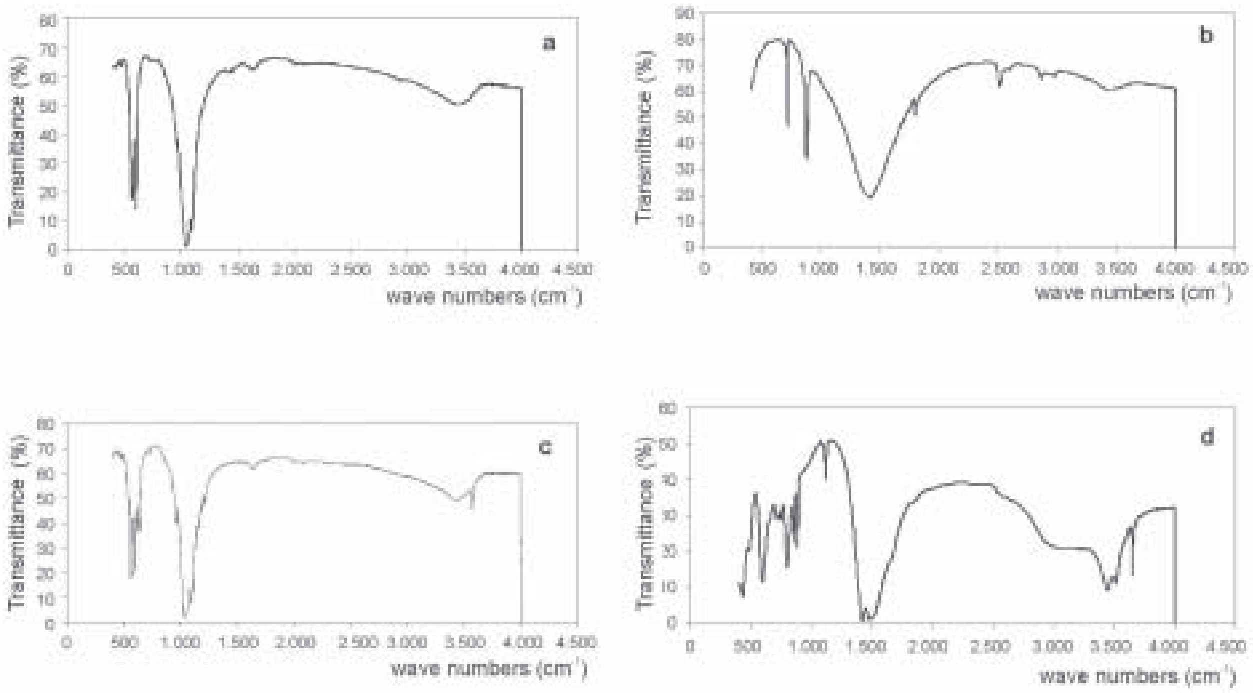

FIGURE 2. References spectra of (**a**) apatite mineral, (**b**) calcium carbonate, (**c**) calcium phosphate and (**d**) magnesium carbonate.

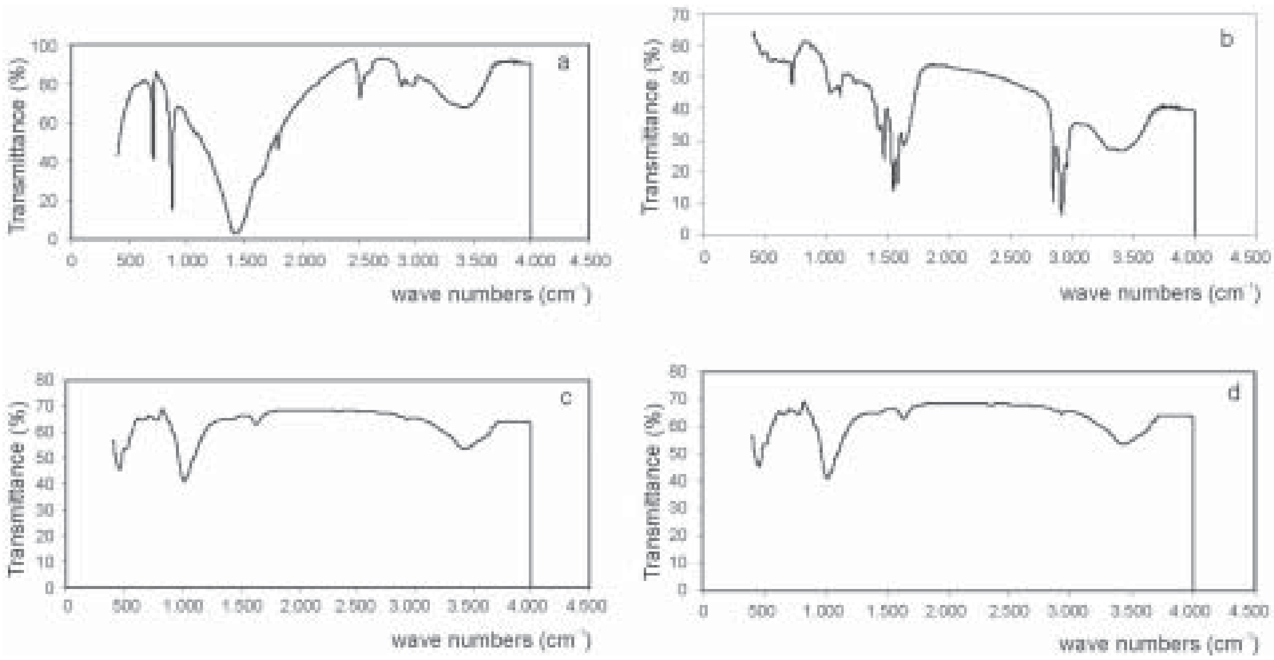

FIGURE 3. Spectra of eggshells (**a**) and excrement (**b**) produced by modern crocodilian, and General Salgado (**c**) and Marília (**d**) sediments.

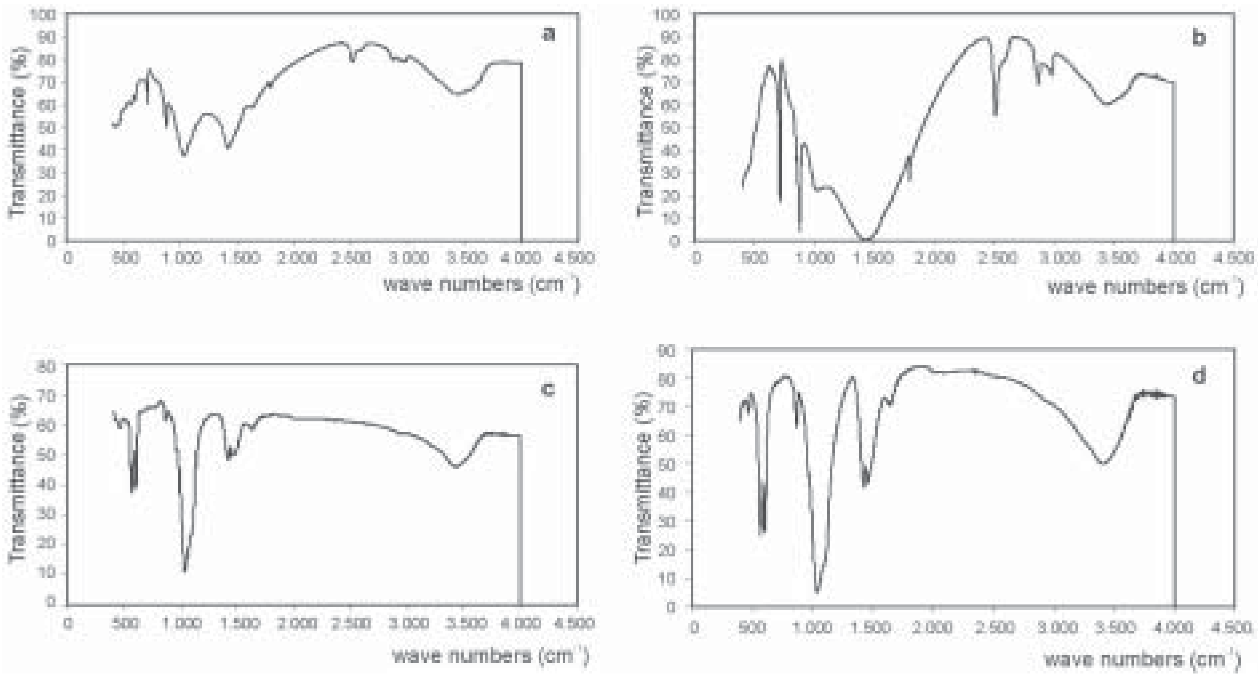

FIGURE 4. Spectra of fossil eggshells (upper graphics) and coprolites (lower graphics) from Marília (**a, c**) and General Salgado (**b, d**) sediments.

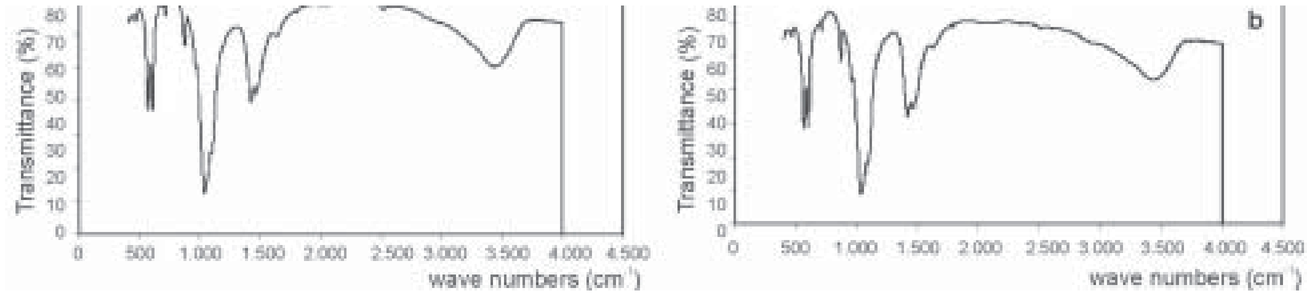

FIGURE 5. Fossil bones of crocodylomorphs from General Salgado UFRJ-DG 286-R (**a**) and Marilia UFRJ-DG107-R (**b**) sediments.

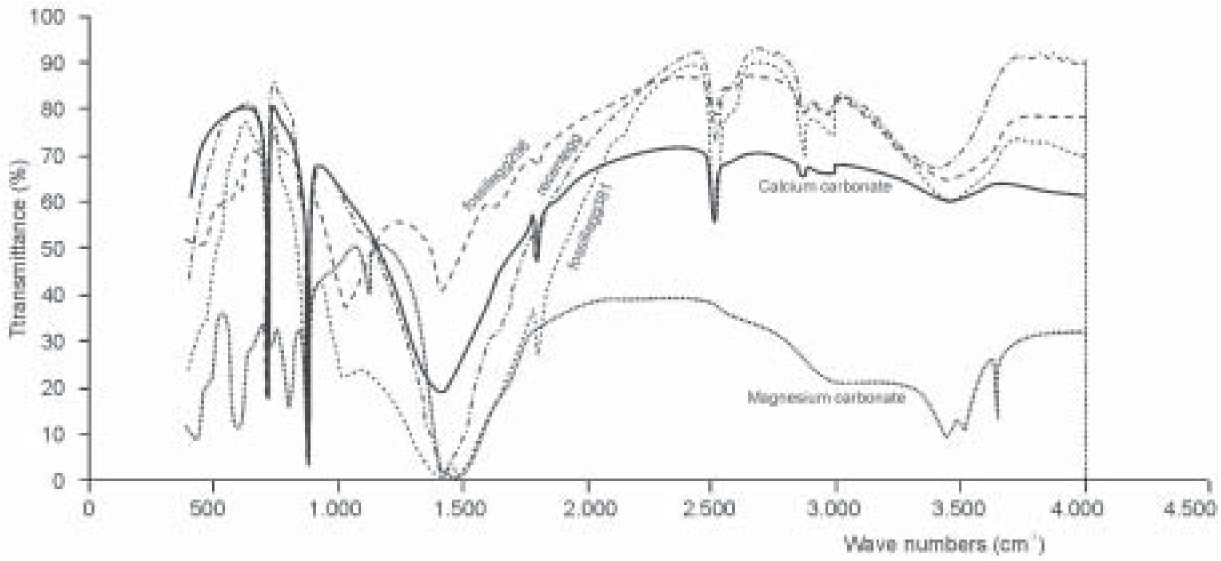

FIGURE 6. Comparative spectra of calcium carbonate, magnesium carbonate, and fresh and fossil eggshells of crocodyliphormes.

The qualitative relationship among the spectra of fossil bones and reference salts showed that the composition of these coprolites (566 and 1,033 cm^{-1}) is also phosphate carbonate and apatite. These coprolite spectra are very similar to found to the fossil bones (566, 604 and 1033 Cm^{-1}) (Figures 7 and 8).

The spectra of fossil and fresh eggshells showed the same absorption bands of calcium carbonate (875 and 1,420 Cm^{-1}), without spectrum similarity with phosphate carbonate and magnesium carbonate.

The spectra of sedimentary matrix varied slightly from location to location (1,637, 1,015, 778 and 460 cm^{-1}), indicating that the sediment composition is the same for the locations.

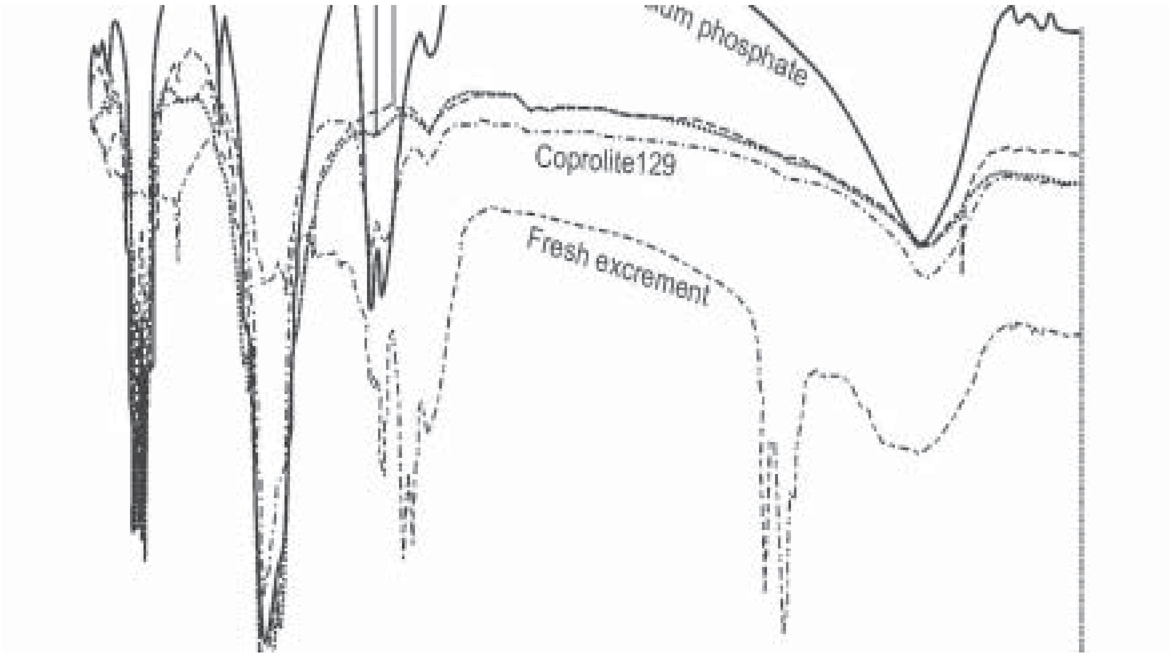

FIGURE 7. Comparative spectra apatite, phosphate carbonate, and fresh excrement and coprolites of crocodyliphormes.

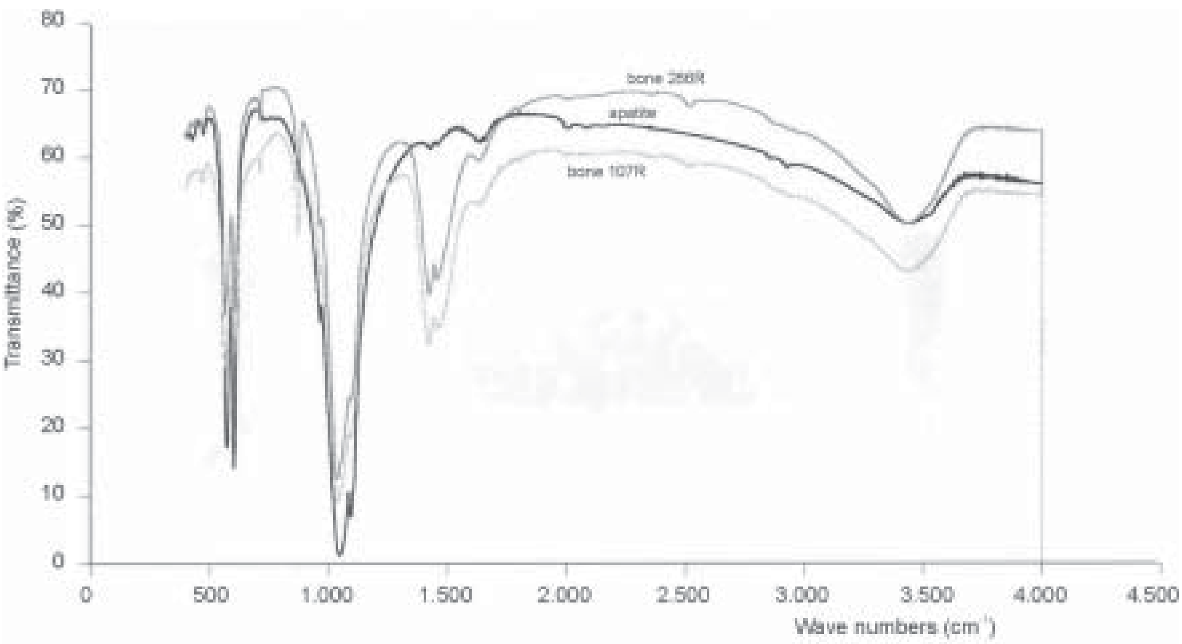

FIGURE 8. Comparative spectra of apatite, phosphate carbonate, and fresh and fossil excrements of crocodyliphormes.

CONCLUSIONS

The absorption bands of fossil bones and coprolites are very similar to apatite and calcium phosphate; the chemical composition is an evidence that the coprolites found in both localities were produced by a carnivorous animal, in this case the crocodilyforms. This same evidence was mentioned by Edwards (1973) and Hallgren (1987), the concentrations of calcium phosphate and apatite presents in fossil bones being similar to the amounts present in coprolites produced by carnivorous animals; the spectra of recent excrement and coprolites also showed the similar absorption bands to calcium phosphate.

Magnesium carbonate is absent in the composition of fossil or recent eggshells and excrements, but is present in fossil bones fragments, what indicates that this compound was not losed due to diagenetic process, and that it is intensively absorbed by digestive process.

As expected, the absorption bands of organic materials and water is higher in fresh excrements and few or absent in recent eggshells; this aspect confirm that the technique can characterize the nature of different organic structures.

The absorption bands of host sediment clearly show that the chemical composition of coprolites, eggshells and fossil bones were not significantly affected by sedimentary matrix.

This work reveals, with comparative analysis of different kinds of fossil elements from the same taxon (Crocodilia), that the infrared analysis technique provides a safe determination and helps in interpretation, independent of age or origin the fossil body.

ACKNOWLEDGMENTS

The author thanks Dr. Leonice Bezerra Coelho, of the Laboratório de Química Inorgânica, Instituto de Química, Universidade Federal do Rio de Janeiro (UFRJ), for the assistance in obtaining the infrared spectra used in this study; Dr. Ismar de Souza Carvalho, responsible of the paleontologic collection of the Departamento de Geologia, Instituto de Geociências, Universidade Federal do Rio de Janeiro (UFRJ); Prof. Valdir Ramos Junior, of the Fundação do Jardim Zoológico do Rio de Janeiro Foundation, Mr. William Nava and Mr. José Tadeu Arruda, for their important assistance in fields works; Fundação de Amparo a Pesquisa do Estado do Rio de Janeiro (FAPERJ) and the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), for the financial support in the field and laboratory works.

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Manuscrito Recebido em: 3 de abril de 2006
Revisado e Aceito em: 7 de julho de 2006