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THERMAL STUDY OF THE FOSSILIZATION PROCESSES OF THE EXTINCT FISHES IN ARARIPE GEOPARK

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The study of fossil materials is very important in the geological and biological researches. They can involve ancient past, evolution or extinction of species, oil prospecting and the understanding of different areas such as: paleoclimate, paleoecology, paleogeography, in addition of climate, environmental changes and life. Araripe Geopark is located in the south area of the Ceará state in the Northeast of Brazil and it provides a general overview of the Earth's History. In this study the vertebral column extinct fish, *Cladocyclus ferox* and its nodule from Santana Formation, Northeast of Brazil, calcite and apatite minerals, and vertebral column of recent fish, *Opisthonema oglinum* were investigated by means of thermal analysis. TG/DTG and DTA curves showed decomposition processes, suggesting water evolution, calcium carbonate and phosphate decomposition and thermal transitions indicated that fossilization processes of fish, carbonaceous material involved the fossil after its death and the organic substance was replaced by inorganic compounds.

Keywords: *fish, fossil, thermal analysis*

Introduction

Fossils provide the only direct evidence of life in the past. The fossil substances are the remainders or traces of once-living things. After an organism is fossilized the remainder can become hard, like a stone. They can be composed of bones, teeth, shells, wood or unaltered material from an organism, such as a frozen mammoth's flesh, bones and its fur. Examples of trace fossils are footprints, leaf impressions, burrows and feces. One of the most common fossil's features is that they are at least 10000 years old. However, not all ancient life was preserved as fossils. In fact, the vast majority simply vanished without traces. The most likely materials to survive fossilization are the hard parts of organisms such as shells and other objects, which were formed from resistant materials, such as coral. To survive, for softer materials or soft-body organisms the conditions must be extremely favourable [1].

Fossils come in a variety of sizes, from minute traces to large skeletons. Trace fossils are clues to pre-existent life; they resulted from the activities or presence of creatures and plants. At the larger end of the scale, the largest body fossils of bones belong to the dinosaurs, which existed between the Triassic and Cretaceous periods.

There are five different ways in which organism can become fossilized:

- Permineralization (Petrification) – This process involves the replacement of the original organic tissues by minerals from the surrounding rock, including silica, calcite or pyrite.
- Unaltered preservation – This occurs when the organism is preserved in its original state and protected from the affects of permineralization. Examples of this include insects that become trapped in tree sap, which later turns to amber. Thermal analytical studies of modern and fossil amber were made by Rodgers and Curie [2] and Ragazzi *et al.* [3].
- Carbonization (Coalification) – These results from removal of all but the carbon elements. Other elements such as hydrogen, oxygen, and nitrogen are removed.
- Authigenic preservation – These fossils are the moulds and casts of organisms, which have dissolved or rotted away, leaving only a trace of their existence.
- Recrystalization – This occurs where crystals form within the original structure, eventually replacing it and resulting in a crystallized copy [4].

Fossilization processes are any kind of fragments, trace or imprint of animals or plants that have been preserved into a rock, sediment or resin since past geologic or pre-historic time. They are found in the Earth's crust usually in a sedimentary basin.

As was mentioned before, the study of fossils is very important in the geological and biological re-

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Fig. 1 Localization map of Araripe Geopark

searches. They can involve life past, evolution of species or extinction, oil prospecting, paleoclimate, paleoecology, paleogeography, climate, environmental changes and life. Araripe Geopark located in the South of Ceará state in the Northeast of Brazil. Figure 1 provides a very unique window into the Earth History [5, 6]. Evolution of organisms is documented in the fossiliferous sediments of lower cretaceous periods about of 120 million years ago.

The geologic Santana formation, in Araripe Geopark is one of the richest fossil deposits of extinct fishes from the low cretaceous. The fossilization processes of these animals are an important scientific challenge that involves large variety of biological, chemical and physical phenomena. The objective of this work is to study the thermal behavior of the fossilization processes of fish from Santana Formation and the results were compared to calcite, apatite and to the vertebral column of fishes.

Experimental

Materials

Vertebral column extinct fish, *Cladocyclus ferox* (Fig. 2) and its nodule originating from Araripe Geopark, located in the South of the Ceará State in the Northeast of Brazil. Samples of calcite and apatite minerals (ordinary minerals) and vertebral column of recent fish *Opisthonema oglinum* were analyzed. The vertebral column of recent fish was clean and separated from the other tissues.

Methods

TG/DTG/DTA measurements

TG and DTA measurements were carried out using a TA Instruments model SDT 2960 temperature range from 30 to 1100°C using 10°C min^{-1} heating rate either in air and in nitrogen atmosphere (flow rate: 120 mL min^{-1}) and sample masses between 10–13 mg for all analysis. The minerals were ground before analysis and vertebral column recent fish was cut.

Fig. 2 Photography of fossil fish nodule showing the vertebral column (scale in cm)

Results and discussion

Figure 3 exhibits the thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) curves for fossilized fish vertebral column, in nitrogen atmosphere. TG and DTG curves showed two decomposition stages.

The first one appeared around 350°C with ~1% of mass loss. This decomposition stage is associated

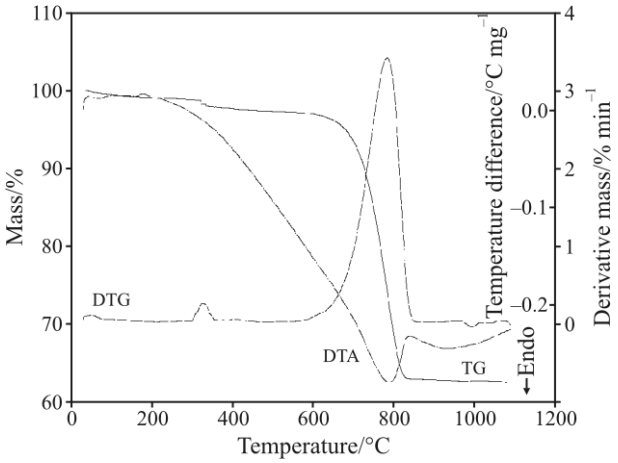

Fig. 3 TG/DTG/DTA curves of fossilized vertebral column fish sample in nitrogen

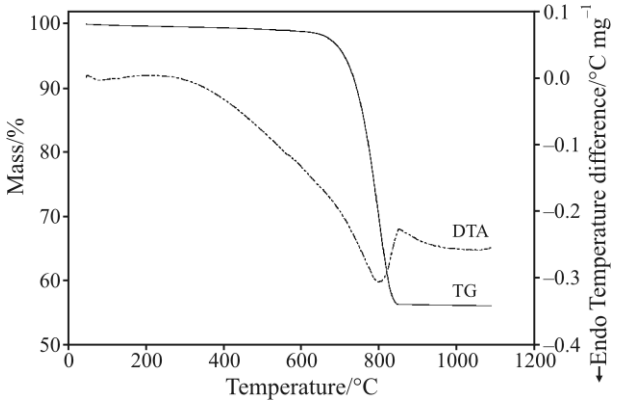

Fig. 4 TG and DTA curves for fossilized fish nodule sample in air

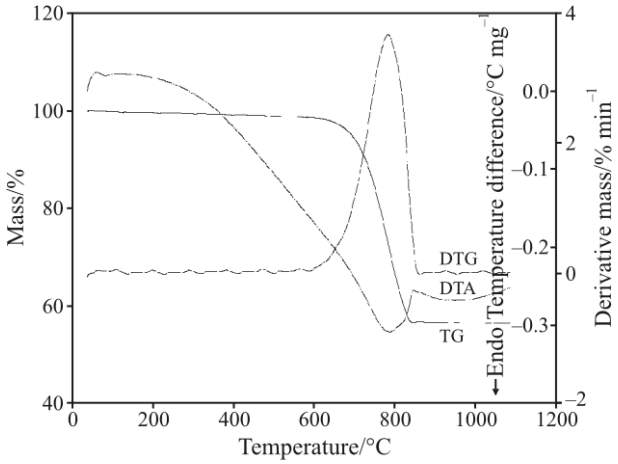

Fig. 5 TG/DTG and DTA analyses for fossilized fish nodule sample in nitrogen

to phosphate and the second one between 600–850°C resulting 37% of mass loss suggests the presence of calcium carbonate [7, 8]. The endotherm peak in the DTA curve around 790°C can be attributed to the release of CO_2.

TG curve of the fossilized fish nodule sample (Fig. 4, recorded in air) presented one decomposition step with 43% of mass loss from 600 to 860°C, probably due to carbonate decomposition. The DTA curve showed two endothermic processes referring to water evaporation around 90°C and decomposition of carbonate around 800°C, with CO_2 formation [9].

Figure 5 shows the TG/DTG/DTA curves in nitrogen. Their shape is very similar to Fig. 4. The decomposition temperature around 600 and 840°C is close to the decomposition temperature of carbonate denying any effect of the purging atmosphere on the decomposition processes.

Figure 6 shows the TG/DTG and DTA records of vertebral column of recent fish. The TG curve exhibited four decomposition stages. The first water loss occurred with 6% of mass loss at 80–100°C, the sec-

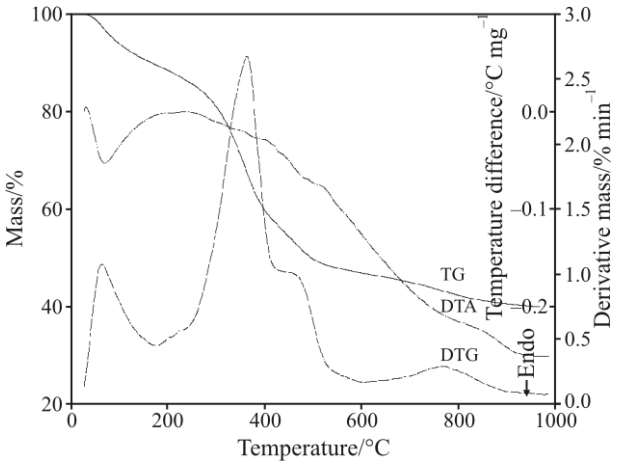

Fig. 6 TG/DTG and DTA curves for vertebral column recent fish in nitrogen

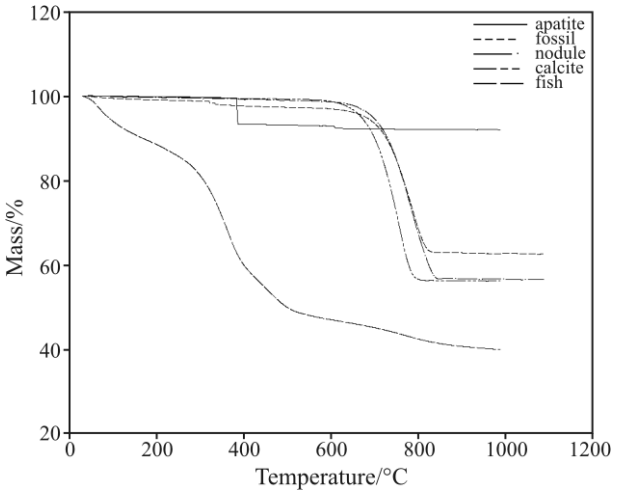

Fig. 7 Comparison of TG curves of fossil, minerals, nodule and vertebral column fish samples

ond stage is between 200–400°C can be attributed to the phosphate decomposition with mass loss of 37%. In the third step in the 400–500°C temperature range probably lipid decomposition with 10% of mass loss takes place. The last stage, with 6% of mass loss between 600–900°C is probably due to the mineral salts' decomposition. DTG curves showed the same events corresponding to the maxima mass loss rate at 90, 380, 430 and 780°C, respectively. DTA curve presents four endothermic events. The first at 80°C and fourth, at 775°C are well defined, but the second and third ones are hardly visible.

Figure 7 depicts comparative TG curves of fossil, nodule, fish, apatite and calcite in nitrogen. The fossil, fish and apatite have decomposition stage around 400°C, while others have not. Calcite, nodule and fossil have decomposition stage around 800°C, while fish and apatite have not. So the first decomposition stage of fossil is similar to fish and second to

calcite due to this the stage can be microorganisms (bacteria) during fossilization process [10] or traces of the original composition of fossil and second stage was correlated to fossilization process.

Conclusions

Thermal analysis can be an effective tool to study fossilization processes from certain kinds of fragment piece, trace of animals or plants that have been preserved into a rock. In this investigation the vertebral column of the extinct fish and its nodule, and the vertebral column of recent fish samples were analyzed, where the curves of TG/DTG and DTA showed various decomposition processes (water, calcium carbonate and phosphate). The thermal transitions indicated carbonaceous material involved the fossil after its death and the organic materials were replaced by inorganic compounds, which were present in the nodule, while vertebral column of the extinct fish had small quantities of phosphate compound. These results could have been produced by bacteria during the fossilization process or it could be traces of the presence of the original organic matter.

Acknowledgements

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References

1 http://www.sdnhm.org/kids/fossils/index.html, 07/13/2007.
2 K. A. Rodgers and S. Curie, Thermochim. Acta, 326 (1999) 143.
3 E. Ragazzi, G. Roghi, A. Giaretta and P. Gianolla, Thermochim. Acta, 404 (2003) 43.
4 www.discoveringfossils.co.uk/Whatisafossil.htm, 07/13/2007.
5 www.geoparkararipe.org, 06/24/2006.
6 R. J. C. Lima, A. A. F. Saraiva, S. L. M. A. de LimaNobre, P. T. C. Freire and J. M. Sasaki, Quim. Nova, 30 (2007) 22.
7 N. Koga, Y. Nakagoe and H. Tanaka, Thermochim. Acta, 318 (1998) 239.
8 D. N. Todor, Thermal Analysis of Minerals, Abacus Press, Kent, England 1976, p. 253.
9 C. G. Mothé and A. D. Azevedo, Análise Térmica de Materiais, IEditora, 1st Ed., SP, Br. 2002, p. 300.
10 I. S. Carvalho, Paleontologia, Editora Interciência, 2nd Ed., Rio de Janeiro, Brasil 2004, p. 861.

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