Physicochemical analysis of Permian coprolites from Brazil

M.I.C. Rodrigues [a], J.H. da Silva [a,b], F. Eroni P. Santos [a], P. Dentzien-Dias [c], J.C. Cisneros [d], A.S. de Menezes [e], P.T.C. Freire [f], B.C. Viana [a,*]

[a] Departamento de Física, Universidade Federal do Piauí, 64049-550 Teresina, PI, Brazil
[b] Campus de Juazeiro do Norte – Universidade Federal do Cariri, 63048-080, Juazeiro do Norte, CE, Brazil
[c] Laboratório Oceanografia Geológica, Universidade Federal do Rio Grande, 96201-900, Rio Grande, RS, Brazil
[d] Centro de Ciências da Natureza – Universidade Federal do Piauí, 64049-550, Teresina, PI, Brazil
[e] Departamento de Física, Universidade Federal do Maranhão, 65080-805, São Luis, MA, Brazil
[f] Departamento de Física, Universidade Federal do Ceará, 60455-970, Fortaleza, CE, Brazil

ARTICLE INFO

ABSTRACT

In this paper we performed the study of two coprolites (fossilized feces) collected from the exposed levels of the Pedra de Fogo Formation, Parnaiba Sedimentary Basin, and Rio do Rasto Formation, Paraná Sedimentary Basin, both of the Palaeozoic era (Permian age). They were characterized using X-ray diffractometry, infrared, Raman and energy dispersive spectroscopy techniques in order to aid our understanding of the processes of fossilization and to discuss issues related to the feeding habits of the animals which generated those coprolites, probably cartilaginous fishes. The results obtained using a multitechnique approach showed that although these coprolites are from different geological formations, 3000 km away from each other, they show the same major crystalline phases and elemental composition. The main phases found were hydroxyapatite, silica, calcite and hematite, which lead to infer that those coprolites were formed under similar conditions and produced by a similar group of carnivore or omnivore fishes.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The study of fossils furnishes valuable informations about the evolution of living beings, the ancient environments (paleogeography, paleoenvironment, and paleoclimatology), and contributes to our knowledge of the mass extinctions that took place in our planet [1]. Thus, the characterization of fossil specimens is important to understand the environmental history of the region where they are found [2]. Trace fossils or ichnofossils are residues of animal and plant activities which inhabited the earth millions of years ago. They are biogenic structures, such as footprints, invertebrate traces, teeth marks, eggs, nests, root marks, tunnels, excavations, feces and urine, being preserved in sedimentary rocks [3]. The fossilization is the result of various physical, chemical and biological process that usually take place in subaquatic environments, such as seas, floodplains, estuaries and lakes, where rapid burial and anoxic conditions prevail. These factors are important to avoid or slow down decomposition of both organisms and biogenic structures. A very important category of trace fossils are the fossilized animal feces, denominated as coprolites [4–6].

Coprolites are structures resulted from heterotrophic activity in the environment. They can occur individually or as aggregates in the sedimentary rocks. Through the analysis of its contents, it is possible to recognize food items that the organisms consumed and even to understand the efficiency of their digestion process [7]. For example, high level of phosphate content indicates carnivorous or omnivorous habits [8,9].

In this context, the present work shows the physicochemical characterization of coprolites from the Pedra de Fogo Formation (PFF), Parnaíba Sedimentary Basin [2,10], which crops out on several areas from the Piauí, Maranhão and Tocantins Brazilian states, and from the Rio do Rasto Formation (RRF), Paraná Sedimentary Basin, which is exposed throughout the Brazilian states of Paraná to Rio Grande do Sul [11]. In order to provide information that may aid the paleontological and geological studies, a multiple characterization approach was carried out. X-ray powder diffractometry (XRD) was used to infer about the main composition and crystalline structure of the fossils. Vibrational spectroscopies (infrared and Raman) may provide information about the chemical functional groups and the identification of the molecular structures from inorganic and organic compounds. Besides, those spectroscopies can provide molecular information from noncrystallized compounds and they can complement XRD analysis. Infrared and Raman measurements offer information about the molecular structure from vibrational modes related to the chemical bonds, but, Raman spectroscopy is nondestructive analysis of the materials surface with no sample preparation. Another no sample preparation technique, energy

* Corresponding author.
E-mail address: bartolomeu@ufpi.edu.br (B.C. Viana).

dispersive spectroscopy (EDS), was used to furnish a rapid elemental (chemical) quantification of the samples [10,12–17]. From these results, it was possible to infer aspects related to the feeding habits of the animals that have produced the coprolites originated from the two different sedimentary basins.

2. Experimental

2.1. Samples

The coprolites occur in large numbers in the PFF [18] and in the RRF [19]. The first one was found in the Pastos Bons municipality, at the type section of the PFF (6°36′12″S; 44°4′29″W), Maranhão state, Parnaíba Basin (Fig. 1(a)). In this site coprolites are abundant [18] and two samples were selected from a collection comprising several specimens collected by Universidade Federal do Piauí in fieldtrips to this locality during 2011–2014. The second ones (two samples) were found in São Gabriel municipality, Rio Grande do Sul state, in a coprolite-rich exposure informally known as "Coproland" [19] (30°20′11″S; 54°19′12″W), RRF, Paraná Basin (Fig. 1(b)). The PFF fossils are considered to be of lower Permian age (Cisuralian Epoch), approx. 278 million years ago, [20], whereas the RRF fossils are regarded as middle Permian age (Guadalupian Epoch), approx. 260–265 million years ago, [21,22]. The chemical composition was obtained by analysis of fragments of the internal and external parts of the fossils.

The coprolites have ovoid format and spiral internal structure. They are isolated from the rock matrix and they are coated by a black or dark layer. An internal spiral structure is visible in transversal section (see Fig. 1). PFF samples present three distinct regions characterized by different colors (red, white and black). It is possible to notice in RRF samples two different regions, named as light red and dark red. Spiral coprolites represent the majority of the coprolites recognized in those geological formations [18,19]. They are fairly common in the fossil record and are considered to be produced by fishes with an intestine having a spiral valve (enterospiral) [23].

2.2. Energy Dispersive Spectroscopy

The EDS composition analysis was performed using a Bruker spectrometer, XFlash system, attached to an electron scanning microscope TESCAN, Vega XMU model. The measurements were performed under vacuum and the analyzed spectral range was from 0 up to 40 keV, with acceleration energy of 30 kV. No sample preparation was necessary for this analysis.

2.3. X-ray Diffractometry

The patterns of X-ray diffraction (XRD) of the powder from different parts of the samples were obtained using a Rigaku diffractometer with Bragg-Brentano geometry. The Co—K radiation was used and operating at 40 kV and 25 mA. The XRD measurements were performed at 10–80° using 0.02° scan of step and 5 s of step time. The crystalline index (CI) was calculated based on a previous work [24].

2.4. Infrared Spectroscopy

Fourier transform infrared (FTIR) spectra were measured by transmittance using the KBr powder method, the ratio of 1:100 of the powder sample: KBr was used and pressed as a pellet. The Fourier transform infrared spectra were measured in the spectral region from 400 to 4000 cm^{-1} using a Bruker spectrometer, Vertex 70 model. The splitting factor (SF) correlated with the apatite crystallinity is calculated following described previously [24].

2.5. Raman Spectroscopy

The Raman spectra were obtained with a mono-grating spectrometer Bruker Senterra with a charge-coupled device (CCD) detection system. The samples were excited using a solid state laser through the 532 and 785 nm wavelengths lines. The resolution was about 3 cm^{-1} and for each spectrum 10 accumulations of 30 s for each spectrum was used. The spectral range investigated covered the 100–1500 cm^{-1}, although we have searched for bands even in the high wavenumber region (up to 3600 cm^{-1}). No sample preparation it was necessary here.

3. Results

In this section we separated the presentation of results in two parts, one related to the PFF coprolite and the other related to RRF one. Initially we have investigated the samples under the scrutiny of the EDS technique to identify what those particular elements and their relative proportions, present in the fossils. The Table 1 shows the results of the chemical elemental atomic percentage, of each region of the PFF coprolite. The presence of O, Si, Al, Fe in the black region suggests, for example, that the main compounds may be silicon oxide, iron oxide and/or aluminosilicate. On the white area the high quantity of O, C and Ca can suggest the presence of calcite and, finally, on the red area, the O and Si amount observed in EDS spectrum indicated, at least, the presence of silicon oxide. The presence of P was identified on the red and white area, as well.

The second technique to investigate the PFF samples was XRD. Powders of each part of the fossil were analyzed and Fig. 2 shows the XRD diffractogram on these different regions, where it is possible to notice the presence of several peaks which were indexed with at least three different crystalline substances. It was identified Fe_2O_3 (hematite), SiO_2 (quartz) and $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite), which are consistent with the chemical elements identified by EDS measurements. Quartz and hematite as the majority crystalline phases on the black area, hydroxyapatite on white area and quartz on red part. The peaks
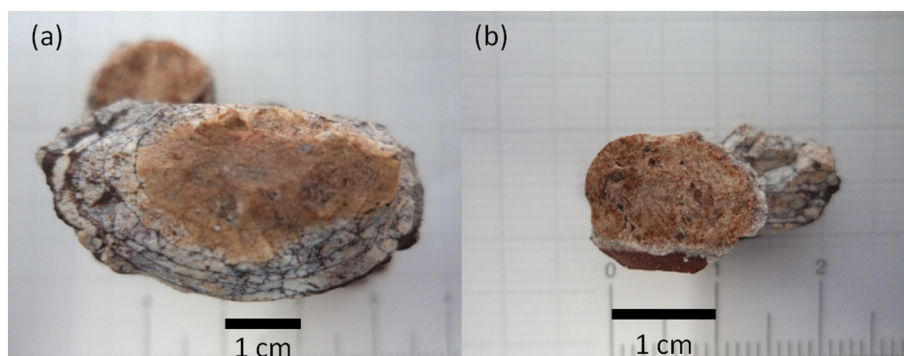

Fig. 1. Optical images of the coprolites and the analyzed regions: a) Coprolites from PFF; b) Coprolites from the RRF.