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Paleometry: A Brand New Area in Brazilian Science

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Paleometry is a promising research field that brings together different areas, such as physics and chemistry, applied to paleobiological issues. In spite of being recognized abroad, it is a new research field in Brazil. The most important characteristic is the application of mostly non-destructive techniques to the study of fossils. This work compiles some paleometrical applications to different geological contexts, such as the synthesis of hard skeleton in *Corumbella werneri*, geochemical aspects about fresh water bivalves from the Bauru Group and the exceptional preservation of arthropods from the Crato Member. Diffuse Reflectance Infrared (DRIFT) and Energy Dispersive X-ray Spectroscopy (EDX) were complementary to elucidate the types of skeletogenesys in *Corumbella*. In the case of the bivalves, DRIFT revealed to be important to elucidate aspects about death and fossilization. Among arthropods, morphological analysis with Scanning Electron Microscopy (SEM) associated with EDX was more profitable to understand fossilization process and paleoenvironmental implications.

Keywords: *paleometry, FTIR, SEM, EDX, calcite, fossilization*

1. Introduction

Paleobiology studies the history and evolution of life on Earth by the means of fossil record. However, this is not an easy task. During the fossilization process, taphonomy (everything that occurs after the death of an organism, until its burial and discovery by the paleontologist)[1] can alter the morphology of the organism, hide important structures and build artifacts that can lead paleontologists to misinterpretations[2-4].

Worldwide, in just a few years, the use of a series of advanced and/or high resolution techniques, mostly non-destructive, has proved to be important for the study of very old and rare well preserved fossils, in order to assist the work of paleontologists. The application of these techniques (*e.g.* Raman and FT-IR spectroscopies[5,6], X ray microCT[7-9], NanoSIMs[10]) to the study of fossils has expanded research in paleobiology and led it to a higher level of sophistication, and it is called paleometry[11].

Inspired in the well established Brazilian archaeometry which studies archaeological, etnographical and the so called patrimonial materials[12-16], the application of paleometrical techniques to the study of many Brazilian fossils is still growing[17-21] and opening new perspectives to deepen our knowledge of the biological affinities and paleoecological aspects. Some exceptionally well-preserved fossils (e.g. the Ediacaran Corumbá Group and the Cretaceous Araripe Basin) have become, in fact, scientific challenges to the development of twenty-first century Brazilian paleobiology. Now, our new paleontology requires, not only the basic description of the oldest forms of life on Earth, but also an understanding and foundation of most modern concepts and methodological assumptions to bring extinct contexts to life. For Brazilian paleontologists, paleometrical techniques have proved to be important, for example, both for the elucidation of the chemical composition of paleoinvertebrate skeletons[22,23], and to understand the processes of fossilization and paleoenvironment in contexts of climate and geochemical changes in the past[20].

In this work, the potential of some of these techniques to the study of invertebrate fossils collected in different and important paleontological sites in Brazil, as seen in Figure 1: *Corumbella werneri* from the Corumbá group (Ediacaran); Unionoida freshwater mollusk from the Bauru Group (Cretaceous); and insects of the Crato Formation from the Araripe Basin (Cretaceous) is presented. The data here compiled is important both to the paleobiological insights

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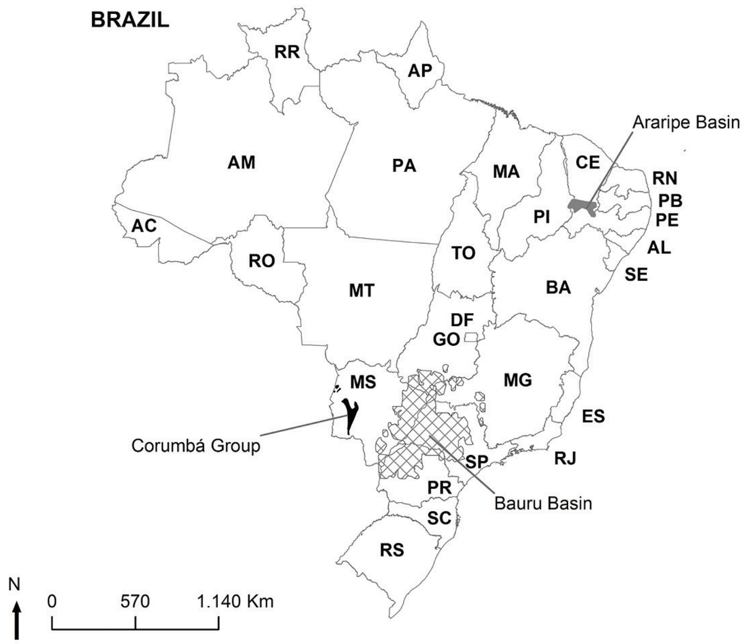


Figure 1. Brazil map with the locations of geological settings where fossils used in this work occur.

and in the field of materials characterization in order to boost paleometry in Brazil.

2. Paleontological Aspects and Motivation

Corumbella werneri (Ediacaran, Corumbá Group) is a fossil preserved in marls and shales. It was considered as an elongated polyhedral tube: a kind of fixed life form of cnidarian medusas that lived ca. 543 million years ago[22]. Their fossils were firstly documented in Ladário and Corumbá, Brazil[24]. Since it was one of the first animals on Earth capable of building a real skeleton, studies with *Corumbella* are important to understand the origin and evolution of skeletonized animals on Earth.

Unionoida mollusks (Cretaceous, Bauru Group) are typically preserved in freshwater sandstones, indicative of energetic processes in paleoenvironmental reconstructions[25]. Our samples were collected in the municipality of Monte Alto, SP, Brazil. Paleometrical analysis has proved to be important to elucidate how these bivalves died and why the vast majority of specimens have articulated valves with sedimentary matrix inside.

The fossil insects from the Crato Formation (Cretaceous, Araripe Basin) are worldwide known for their high level of preservation in carbonates, including three-dimensional specimens with soft tissues preserved[26-28]. These fossils have important paleobiological and paleoenvironmental information and it is, therefore, crucial to understand the taphonomic processes that led to their exceptional preservation. Despite having been briefly discussed in previous studies[26,29], the taphonomy of the insects of the Crato Formation is still an unresolved question.

3. Experimental

The fossils have been characterized at the Laboratory of Characterization of Materials (LMCMat) at UNESP (Sorocaba, Brazil), in collaboration with the Group of Plasmas and Materials and at the Brazilian Nanotechnology National Laboratory (LNNano) at CNPEM (Campinas, Brazil).

The chemical composition of *Corumbella werneri*, (Figure 2a) and the Unionoida freshwater mollusk (Figure 2b) were investigated by using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT) at LMCMat. DRIFT analysis revealed to be the most appropriate for IR spectroscopy due to the small amount of available samples and to the configuration of the spectrometer sample holder. For the analysis, grated powder of the fossils and the respective rock matrices were collected and dried at 50 °C. The dried powder was placed in a cylindrical sample cup that was partially filled with KBr powder, forming an upper layer with the material of interest. According to J. Ji et al.[30], the use of unmixed layers saves a significant amount of time and does not interfere with the sensitivity to carbonates and sandstones, which are the main components in the analyzed fossils. The ratio of the amount of sample and KBr powder was kept approximately to 1:9. The layers were carefully pressed into the cup for the measurement of the sample spectra and another sample cup filled with only KBr powder was used for the measurement of the background spectrum. The analyses were carried out with a *Jasco FT-IR 410* spectrometer in the range of 600-4000 cm^{-1}, with a resolution of 4 cm^{-1} and average of 100 scans.

The micromorphology characterization of *Corumbella werneri* was performed at LNNano, with an electron

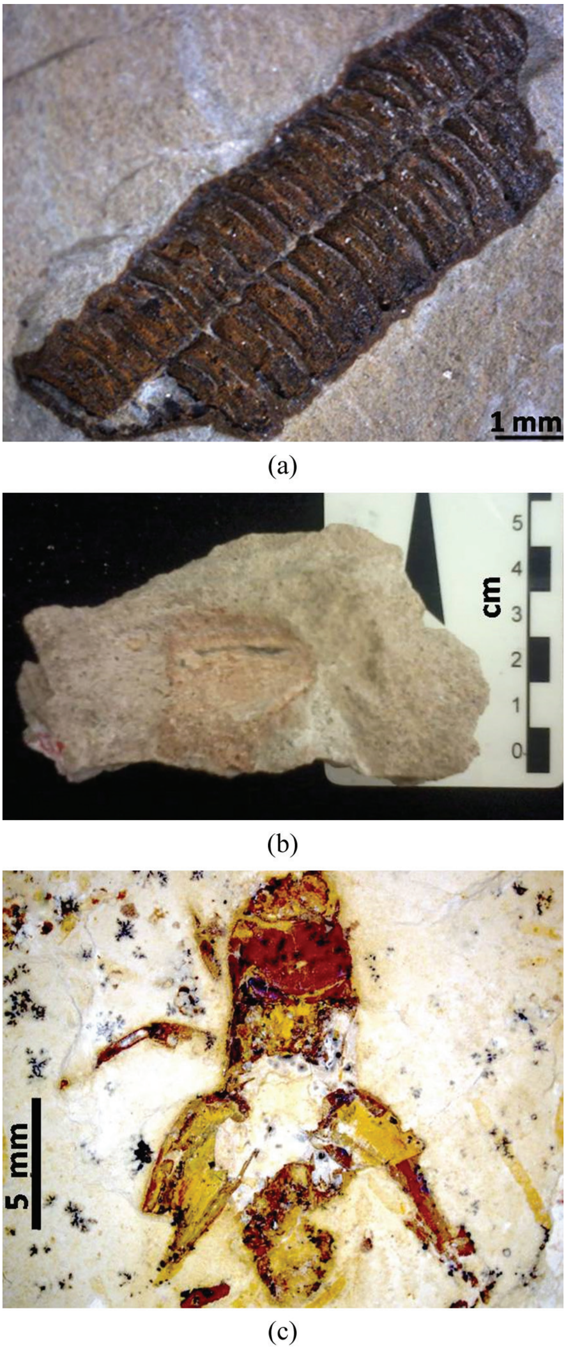


Figure 2. Studied fossils: (a) *Corumbella werneri* (Ediacaran, Corumbá Group); (b) Unionoida freshwater mollusk (Cretaceous, Bauru Group). (c) Cricket (Cretaceous, Araripe Basin) from IGc/USP collection, specimen n. GP/1E-7105.

microscope *FEI Quanta 650 FE* in the mode of secondary electrons detection, with acceleration voltages of 10 kV. Energy Dispersive X-ray Spectroscopy (EDX) was also carried out using an *X-Max* detector in semi-quantitative and mapping mode, in order to identify the distribution of chemical elements and compare it to FTIR results.

The fossil cricket of the Crato Formation (Figure 2c) was kindly lent to the researchers by IGc/USP collection (specimen n. GP/1E-7105). Its ultrastructure was characterized at LMCMat, analyzed by Scanning Electron Microscopy (SEM), with a *Jeol JSM6010* microscope, with acceleration voltage of 10 kV[20]. The fossil samples were coated with Au/Pd thin layer in order to improve the quality of the micrographs. EDX measurements with a *Jeol Dry SD Hyper Detector* were also applied to the sample, in order to identify the chemical composition of the observed structures on the fossil surface and inside the specimen[20].

4. Results and Discussion

4.1. Corumbella werneri

Diffuse reflectance analyses, in Figure 3, give us information about the ultrastructure of the carapace of *Corumbella werneri* and the respective rock matrix. The main IR bands are indicated in Figure 3 and correspond to calcite[30-32]. It is worth pointing out that in the reflectance spectrum, the weak IR bands appear stronger than expected for the absorption and transmission spectra. This stems from the fact that in reflectance spectra there is no linear relationship between band intensity and concentration (as it occurs in transmission), and quantitative analyses by the DRIFT method are therefore rather complicated. The band in 2509 cm^{-1}, for example, is described as very weak and weak in the transmission spectra presented in works of Miller and Wilkins[33] and Huang and Kerr[31], respectively, while it can be considered strong in our work in consistence with the reflectance data presented by Ji et al.[30]. Since the quantitative approach is not necessary at this point of our study, our research will focus on qualitative analysis that can provide paleobiologists with new important information.

Table 1 presents the comparison between the IR reflectance bands of the fossil of *C. werneri* and its rock matrix (Figure 3). The bands in the IR region from 600 to 1500 cm^{-1} occur due to the four fundamental modes of vibration of the carbonate ion (CO_3^{-2}): ν_1 is the symmetrical stretching of CO (ν_s); ν_2 is the out-of-plane bending of CO_3 (γ); ν_3 is the asymmetrical stretching of CO (ν_{as}); and ν_4 is the in-plane bending of OCO (δ)[31,34] . The ν_1 mode should be inactive in FTIR spectra due to the symmetry of the molecule[31,35], but since the studied sample (rock + fossil) presents several other minor constituents and impurities (common in sedimentary rocks), it is possible that bands at 1010 cm^{-1} for the fossil and 1160 cm^{-1} for the rock matrix are due to the ν_1 mode, which theoretically would occur at 1087 cm^{-1}. The vibrations at 875 and 711 cm^{-1} correspond to out-of-plane and in-plane bending, respectively. Both are observed in the carapace reflectance spectrum, but not in the rock matrix spectrum, despite being a marl (kind of shale carbonate rich rock). From the difference in spectra of the fossil and the rock, we can wonder if the synthesis of this hard exoskeleton leads to higher concentrations of the calcite in the carapace than in the surrounding rock medium. Finally, the asymmetrical stretching mode occurs at 1452 cm^{-1} as a broad band in the fossil reflectance spectrum with no obvious correspondent band in the rock spectrum. This band is actually a double degenerated band that is observed for pure materials as a doublet. The mixture of minor components in the matrix can be responsible for the

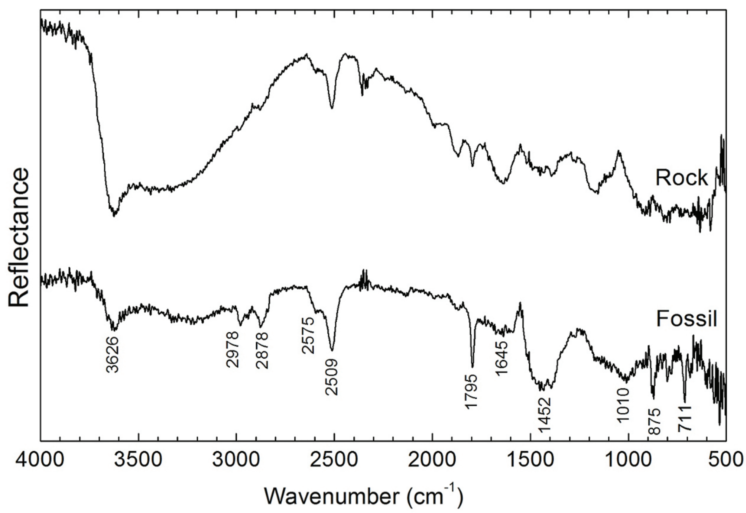


Figure 3. Diffuse reflectance infrared spectra of *Corumbella werneri* carapace and rock matrix. The positions of the absorption bands are indicated in the figure.

Table 1. Comparison of IR reflectance bands for analyzed fossils and their rock matrices.

Wavenumber (cm^{-1})			
C. werneri	**matrix**	**molusk**	**matrix**
3626	3622	3617	3668
2978	2983	2948	*
2878	2878	2877	*
2575	2594	2588	*
2509	2511	2508	*
---	2360	2362	*
1795	1796	*	*
1645	1641	*	*
1452	*	*	*
1010	1160	*	*
875	*	863-836	*
711	---	700	*

*refers to undistinguished bands of continuous noise.

enlargement of each line of the doublet, in a manner that they cannot be interpreted. The other observed bands of IR Reflectance are all regarded as vibrations of the carbonate ion in overtone modes and combinations of the fundamental modes[30,36]. Most of them appear both in the reflectance spectra of the *Corumbella* and in the rock with different relative intensities.

On the other hand, the large shoulders observed in 1000-1200 cm^{-1} and 1600-1800 cm^{-1} can be putative chitin, when compared with the reflectance data of analyzed chitin from black corals[37]. These shoulders are clearly not present in the spectrum of rock matrix, hence the assignment and interpretation of these will be further investigated in future work.

The EDX mapping (Figure 4) supports the assumption that there is higher concentration of calcium (attributed to calcite) in the carapace of *Corumbella* in comparison with the rock matrix. It is also possible to see in Figure 4c, that Fe atoms are more concentrated (density in gray scale) in the rock than in the fossil. Si, Al and O atoms were also detected by EDX and presented the same surface distribution as Fe atoms. The existence of O is related to the oxides present in the matrix. On the other hand, in Figure 4d, it is seen that Ca ions present a higher concentration in the carapace, with C atoms accompanying this tendency. The presence of Ca and C in the carapace denotes the presence of calcite in an organic carapace and, together with IR reflectance analysis, gives us evidence of a biomineralized exoskeleton.

As a technique for elemental characterization, EDX is important to complement IR Reflectance or FTIR Absorption spectroscopy. Moreover, the EDX mapping analysis allows the investigation of the distribution of element concentration with higher resolution than it could be achieved with IR spectroscopy.

The collected results from DRIFT and EDX spectroscopies reinforce, if not an entirely organic tegument[23], at least, a weakly mineralized *Corumbella* carapace[22], among one of the first skeletonized animals. The evolution of animal skeletogenesis could be linked to environmental changes, such as the oceanic chemistry, as well as selective pressures correlated with the appearance of new ecological relations, such as predator/prey ones[38].

4.2. Unionoida bivalve

The same approach previously described was applied to the bivalve. The identified IR reflectance bands are indicated in the spectrum in Figure 5 and listed in Table 1.

It is noticeable that the IR spectrum of rock does not contain any information about its chemical composition, since the continuous noise is quite high when compared to candidates to reflection bands. This occurs due to the fact that sedimentary rocks, such as sandstones, can be composed of different kinds of minerals and organic matter.

The IR reflectance spectrum of the fossil, on the other hand, presents bands that are attributed to calcite, as seen in Table 1. Since the reddish internal part of the mollusk should correspond to soft tissue fossilized in the interior

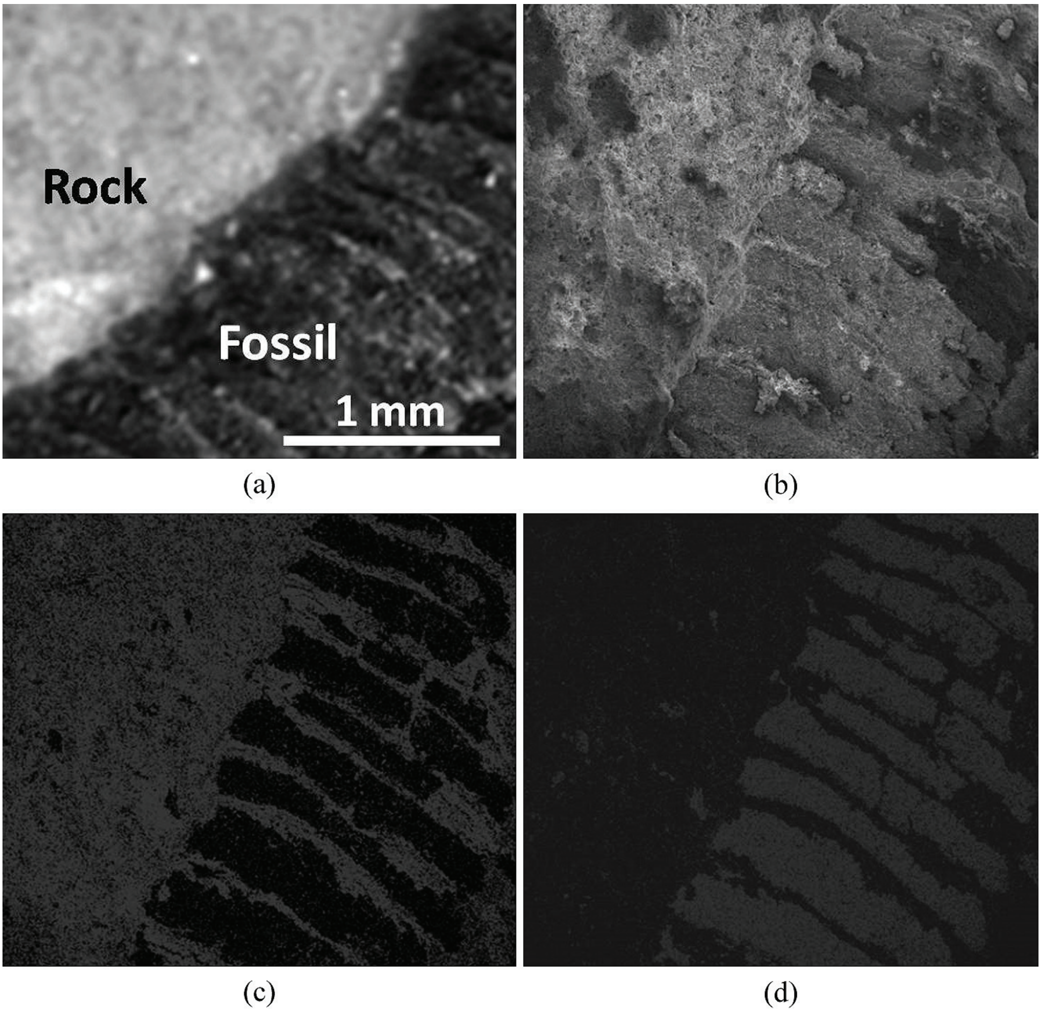


Figure 4. SEM/EDX analysis of *Corumbella werneri*: (a) Image of the analyzed portion of carapace and rock matrix. The scale in photograph refers to the all four images. (b) SEM micrograph of fossil and rock; (c) EDX map of the distribution of Fe on the sample; (d) EDX map of the distribution of Ca on the sample. For the figures (c) and (d), the lighter spots indicate higher concentration of elements, while the dark regions indicate the absence of the element.

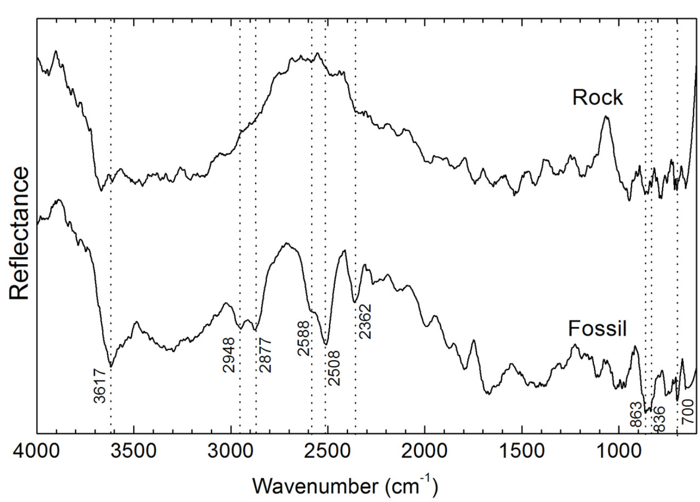
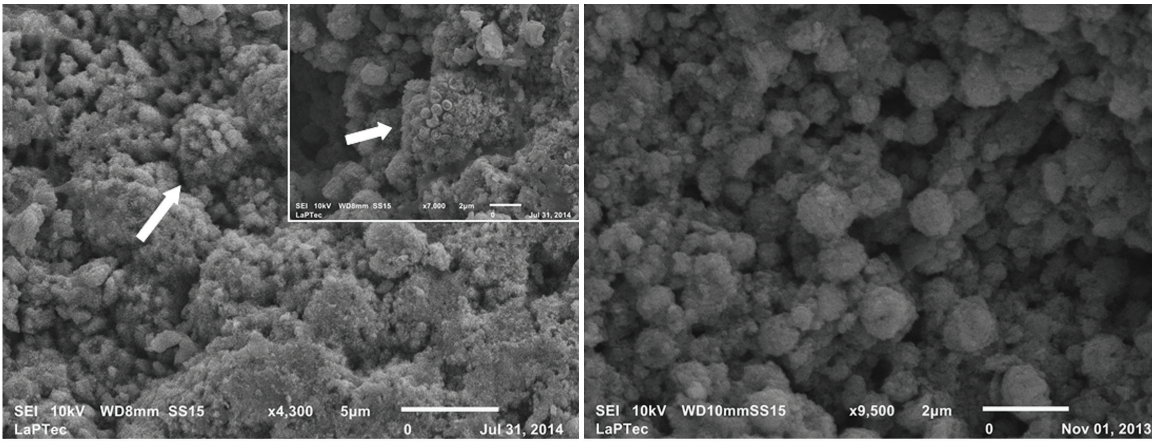


Figure 5. Diffuse reflectance infrared spectra of inner part of Unionoida bivalve and surround rock matrix. The positions of absorption bands that can be distinguish of the noise of spectrum of fossil are indicated in the figure.



(a) (b)

Figure 6. Photomicrographs of the minerals which constitute the fossils from the Crato Formation. (a) Exoskeleton replaced by pseudomorphs of framboidal pyrite (indicated by arrow; detail of a well preserved pseudomorph). (b) Interior of the fossil, with preserved framboidal pyrite pseudomorps.

of the shell, the presence of calcite suggests models of fossilization via incorporation of calcite available in the internal part of the shell[39,40]. This can occur when the specimen is fossilized with closed and articulated valves, creating an internal system isolated from the environment. After death, in decomposition, closed valves may have solubilized, and calcite might have been trapped in the sediment within the valves.

4.3. Insect of the Crato Formation

SEM analysis of the fossil cricket from the Crato Formation was performed in order to investigate the characteristics of the minerals that replaced the original organic matter. It was found that the texture of the exoskeleton or carapace (Figure 6a) is different from the inner part of the specimen (Figure 6b). While the exoskeleton consists of pseudomorphs of framboidal pyrite >5µm in diameter, the inner portion of the fossil is filled with framboidal pyrite pseudomorphs with ca. 1µm of diameter. Pyrite is a metallic mineral with chemical formula FeS_2 (iron sulfide).The observed grains are interpreted as being pseudomorphs since their EDX analysis (Table 2) does not show the presence of sulfur in chemical composition. The pseudomorphs are covered with pliable structures here interpreted as mineralized extracellular polymeric substance (EPS) (Figure 7).

Data presented in Table 2, should be interpreted as an estimation of the chemical composition of the exoskeleton and the inner part of the fossil. Despite not being a quantitative analysis, the data gives valuable information about the presence or absence of key elements that can be associated with taphonomic and environmental processes.

EDX data supports that both external and internal portions of the fossils have iron and oxygen, suggesting that pyrite has been replaced by iron oxides/hydroxides due to weathering[20]. Furthermore, the inner part of the insects also presents small amounts of phosphorous and magnesium, that are not observed in the exoskeleton. These elements must be further investigated since there are is no definite evidence

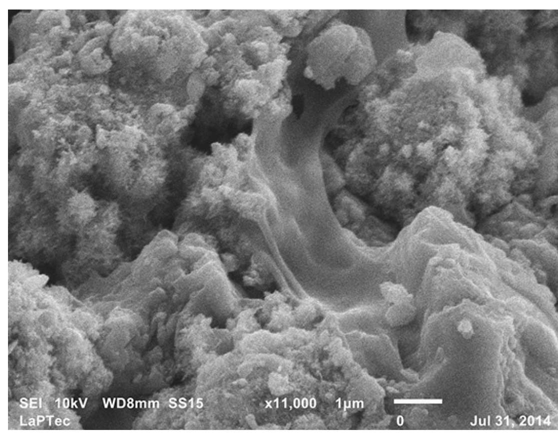


Figure 7. Pseudomorphs of framboidal pyrite covered by mineralized EPS.

Table 2. Estimated chemical composition of the exoskeleton and inner part of the insect of Crato Formation. Data were obtained with EDX in semi-quantitative mode. The errors were automatic calculated by the analysis software.

	Atomic composition (%)	
element	**exoskeleton**	**inner part**
C	23.735 ± 0.010	24.697 ± 0.010
O	56.60 ± 0.04	60.63 ± 0.05
Na	0.575 ± 0.021	0.523 ± 0.021
Mg	---	0.369 ± 0.021
Al	0.914 ± 0.021	0.503 ± 0.021
Si	2.14 ± 0.03	1.067 ± 0.021
P	---	1.78 ± 0.03
Ca	5.51 ± 0.06	8.29 ± 0.07
Fe	10.533 ± 0.020	2.13 ± 0.13

that could relate them with intrinsic characteristics of the organisms neither extrinsic conditions of the environment or with taphonomic processes[41].

The textural differences verified between the carapace and the inner portion of the fossil might occur due to distinct mechanisms of fossilization. The presence of framboidal pyrite pseudomorphs, replacing and infilling the fossil , which possibly indicates the oxidation of previously precipitated pyrite framboids, as well as their coating by EPS, strongly suggest the activity of sulfate reducing bacteria during diagenesis, as suggested elsewhere[29]. The very small size of the minerals may also account for the high degree of fidelity of preservation of the Crato Formation fossil insects[20].

5. Conclusion and Perspective

IR Reflectance and SEM/EDX analysis were successfully applied to the study of Brazilian fossils from different geological contexts contributing to the progress and broadening of paleometry in Brazil. The use of IR Reflectance instead of Transmittance allowed the observation of the bands that would appear weaker in transmission/absorption modes, which can be a great advantage for complex materials such as rocks and fossils. The EDX mapping showed to be an important complementary technique to: (a) Reflectance spectroscopy, bringing information about the distribution of elements on fossil surface enabling even higher resolution with IR analysis; (b) SEM morphological characterization, allowing elemental analysis of specific biological structures. Interpretative results contributed to clarify outstanding questions still open in paleobiology and in taphonomy, such as: (1) the understanding of evolutionary and geochemical trends that led to the origin and diversification of skeletonized animals such as the *Corumbella*; (2) the establishment of specific conditions that culminated in different types of fossilization in high energy environments, such as the Bauru Group; (3) the interpretation and comprehension of exceptional and rare well preserved soft parts, just like the case of insects from the Crato Formation. In this sense, paleometry has shed new light on material sciences studies and has opened a window to a brand new and exciting past for paleobiologists.

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