X-ray diffraction studies of the structure of fossilized dinosaur eggshells from Mesozoic of Portugal (Lourinhã Formation)

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We have been using Synchrotron Radiation-based Micro-Computed Tomography (SR- μ CT) for the characterization of fossilized eggshells from the collection of the Museu da Lourinhã, Portugal [1,2]. Here we report the use of Synchrotron Radiation-based X-ray Diffraction (SR-XRD) in the study of these fossils. The combination of SR- μ CT and SR-XRD allowed us to assess the diagenetic alteration of several fossilized eggshells, mainly dinosaur eggshells, from the Mesozoic of Portugal.

Experimental

The experiments were carried out at the High Energy Materials Science beamline (HEMS) at PETRA III. This beamline offers the opportunity to investigate fine structural details (high flux in parallel beam to increase resolution and enough signal in the small gauge volumes). SR-XRD data were acquired in transmission mode (with an image plate MAR345) using a beam spot of 100 μ m in vertical and 300 μ m in horizontal with 87 keV energy (the eggshell fragments were mounted on the sample holder with the outer and inner shell surfaces nearly parallel to beam). The samples were measured starting from the outer surface to the inner surface of the shell, along a "line" perpendicular to these surfaces (width = 300 μ m), every 100 μ m with an acquisition time of 1s.

Results

X-ray powder diffraction can be useful to determine if eggshells had undergone diagenetic alteration. However, a detailed study of their structure from the outer to the inner surface is required in order to "map" mineralogical alterations. Additionally, the analysis of SR- μ CT data together with data obtained by XRD provides valuable information. For example, Fig. 1 shows a microtomographic image of a dinosaur eggshell fragment collected from the locality of Porto das Barcas, which has been attributed to the megalosaurid theropod *Torvosaurus sp.* [3]. The eggshells are highly porous and, thus, indicative of eggs buried for incubation within the substrate. All eggshells analyzed have equivalent pore density, which may suggest that all eggs were buried under a homogenous incubating medium.



Figure 1: Fossilized eggshell fragment collected from the locality of Porto das Barcas (thickness ≈ 1.2 mm).

Microscopy and SR-µCT data suggested that an external zone resembling an additional layer may be present in the eggshells. However, SR-XRD data collected for the external and internal surface zones of the eggshell fragments show the presence of quartz and phyllosilicates (sediment from the surrounding matrix). SR-XRD patterns obtained for an eggshell fragment studied at HEMS are presented in Fig. 2. Moreover, SR-XRD data indicate that pore-filling sediment is composed mainly of phyllosilicates. Also, SR-XRD data show that the major compound of the eggshells is calcite. Judging by the complex eggshell pore structure and depositional environment, the nesting environment is inferred to have been in highly moisturized conditions.



Figure 2: SR-XRD patterns obtained for an eggshell from the locality of Porto das Barcas. The data were collected at the topmost zone (external surface zone), at the middle and at the bottommost zone (internal surface zone) of the eggshell. The data were acquired in transmission mode (beam closely parallel to the outer/inner surfaces of the eggshell).

Thus, as shown in the previous example, SR-XRD is a very useful technique for the characterization of fossilized eggshells in order to assess the extension of diagenesis. Furthermore, the nature of the sediments in which eggshells are deposited may allow inferring the probable environmental conditions in which extinct animals lived.

References

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