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THERMAL REACTIVITY OF FOSSILIZED DINOSAUR EGGSHELLS

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Abstract

The thermal reactivity of fossilized/petrified dinosaur eggshells excavated in China, Argentina and France has been studied by means of thermal analysis/mass spectrometry (TG-MS), X-ray diffractometry (XRD) and analytical scanning electron microscopy (SEM-EDX). The results provide more detailed information on the properties of these fossil materials and therefore allow an improved typology of this most remarkable family of creatures.

Keywords: combined thermal analysis/mass spectrometry, dinosaur eggshells, phase analysis, scanning electron microscopy, thermal reactivity, X-ray diffraction

Introduction

The discovery of petrified eggshells, eggs and nest colonies of various dinosaurs at various locations provided a remarkable boost for the elucidation of the living conditions of these best known fossil animals [1, 2]. There are, however, only a few investigations on the different chemical properties of these eggshell materials. Of course, they have suffered fundamental geogenic transformations, but the observed partial conservation of the shape, of the preliminary determination of the chemical composition and the microscopic texture has lead to an improved typology. Thus, it is possible to compare the actual samples with the specimens found in the sites listed below:

Worldwide locations, where fossil dinosaur eggshells have been found

Continent	Country	Number of sites
Africa	South Africa, Mozambique	2
Asia	China, Mongolia, India	139
Europe	France, Germany, Spain	39
North America	USA (Utah, Arizona)	37
South America	Argentina	12

More detailed, comparative studies on the chemical composition, the textural features, as well as the thermal reactivity, provide further information and further in-

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sights into the life and time of these fascinating creatures. Therefore, we set out to compare samples of petrified dinosaur eggshells stemming from locations in China, France and Argentina. As methods and means of investigations, we chose X-ray diffractometry, combined thermogravimetry/mass spectrometry and analytical scanning electron microscopy.

Experimental

Fragments of excavated eggshells stemming from three locations have been investigated. From Argentina, fragments of the extremely rare petrified eggshell of the saltasaur, first discovered in 1970 in the province Salta, Northwest Argentina, have been characterized. The saltasaur species belongs to the medium sized sauropods, which lived at the beginning of the cretaceous period, 130 million years ago. From France, fragments of eggshells of hypselosaur, a member of the apatosaur family, has been investigated. This species lived 66 million years ago, i.e. at the very end of the dinosaur era. The actual sample was collected in Aix-en-Provence, South France. The eggs of the 12 metre long hypselosaur, first found as early as in 1850 in Fuveau, Provence, but at that time not yet typologised, reach a volume of 3.5 liters and a diameter of 0.25 to 0.30 metre. The third sample has been excavated in Hubei, Central China. It stems of amargasaur, a sauropod species which lived 100 million years ago and belongs to the earliest of the late Chinese Cretaceous deposits. Additional samples were investigated with respect to the morphological and textural features of the shell structures. These data were only used for the typological classification.

For the comparative phase analysis X-ray diffraction patterns were obtained from a Guinier-IV camera working with CuK_α radiation. As internal standards, analytical grade calcite and quartz were used.

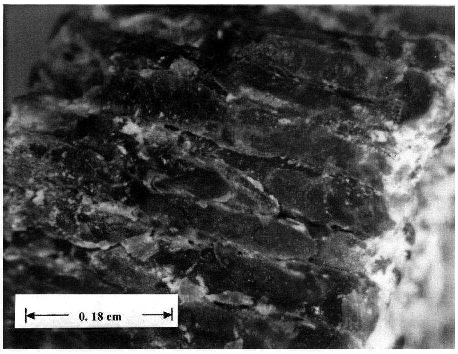

Fig. 1 Light-microscopic image of a section through the petrified eggshell of a saltasaur (Salta, Argentina, 130 million years ago). The dendro- or tubospherulitic morphology is a typical construction scheme of the eggshells of sauropods

The thermogravimetric/mass spectrometric measurements were performed on the new Mettler-Toledo TGA/SDTA 851^e (Mettler-Toledo GmbH, Schwerzenbach, Switzerland) module, coupled to a Balzers ThermoStar mass spectrometer (Balzers

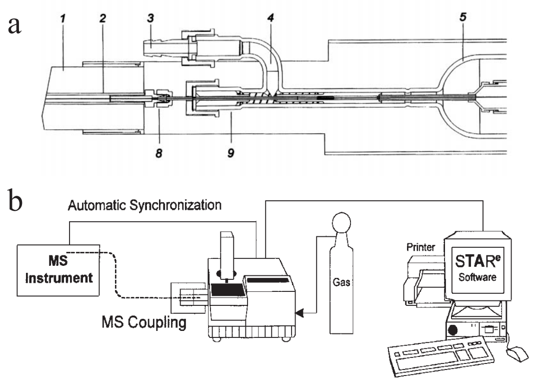

Fig. 2 a) Schematic view of the Mettler Toledo TGA/SDTA^e module coupled to the Balzers Thermostar mass spectrometer unit; b) Sectional view of the TG-MS coupling system: 1 – hose for heating; 2 – teflon tubing; 3 – plastic olive; 4 – gas outlet; 5 – fused silica jacket; 8 – clamped joint; 9 – coupling outlet)

AG, Balzers, Liechtenstein) (Fig. 2). The samples were placed in platinum crucibles without lids, and heated in air at 10°C min^{-1}. The volatile products were sampled in close proximity to the crucible in the thermobalance furnace and transferred to the mass spectrometer through a heated quartz-capillary kept at a constant temperature of 110°C. The data evaluation was performed with the Quadstar 421 Window^{TM} 3.1 process control module.

The scanning electron micrographs and the electron dispersive analysis of X-rays were obtained from a Philips SEM 515 (Philips, Eindhoven, The Netherlands) equipped with a Tracorn Northern 5400, EDX system, as well as a Philips ESEM XL30 FEG and EDX analytical module with a Si(Li)-type detector equipped with a Super-UTW (sapphire series) (FEI and Philips, Eindhoven, The Netherlands). In Fig. 1, a light-microscopic image of a section through a petrified eggshell is presented. It can be seen that the thickness reaches around 5 mm and – although massive chemical transformations took place during the petrification – the microtexture (see also scanning electron micrographs, below) and the stratification can be clearly identified. The morphological features are typical for dendro- or tubospherulitic construction schemes, which have been found for many sauropod eggshells.

Results and discussion

It is well known from geogenic processes that, depending on the local or regional historical processes, biogenic materials undergo specific transformations, i.e. in general terms fossilization and petrification take place. The detailed physico-chemical and geochemical investigation of fossil artifacts allows differentiation into the most important calcification and silification processes. There are other, less abundant fossil products formed by pyritization etc. These transformations are mostly specified by taphonomists and biostratonomists [5].

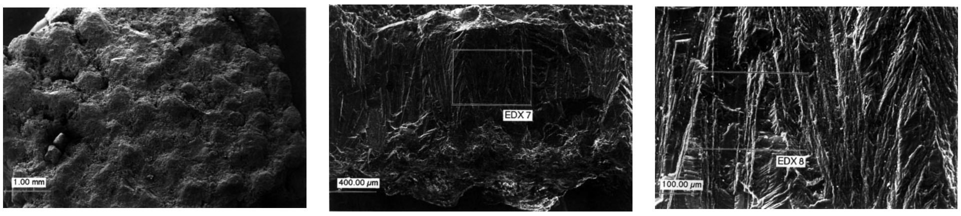

Fig. 3 Scanning electron micrographs showing the surface texture of a hypselosaur eggshell found in Provence, France (a). As EDX measurements reveal, the outer surface of this sample is made up of a mixture of phases, where silica and calcite coexist with other phases, which are either magnesium-aluminum silicates or dolomite (b). The inner part of the shell is made up of pure calcite (c)

We first focussed on the phase analysis of the investigated samples. The evaluation of X-ray diffraction patterns allowed us to identify calcite and quartz as principal phases. Detailed analyses gave evidence for small amounts of other phases which could either be dolomite or a Mg/Al-silicate.

The microstructural investigations by analytical scanning electron microscopy gave evidence that the morphology and the texture, as well as the chemical composition (determined by EDX analysis) of the studied samples vary remarkably. Based on a typology of dinosaur eggshell textures [2], the three samples could be attributed to the dinosaur species mentioned in this chapter. In Fig. 3a, the outer surface of the eggshell of a hypselosaur (Provence, France, 66 million years ago) is shown. Detailed investigations are presented in Fig. 3b and 3c: whereas the morphological features can be interpreted by a dendritic construction scheme typical for an apatosaur, i.e. the sauropod family, the analytical measurements show that the larger inner part of the shell is made up of pure calcite, the outer skin, is however of silica and further Mg–Al–Si–O phase(s).

In Fig. 4a, the texture of the 130 million year old eggshell fragment of a saltasaur (Argentina) is presented. The rather undefined texture cannot be directly typologized, i.e. the geochemical transformations do not allow the observation of the characteristic features as seen for the hypselosaur or saltasaur eggs. As Fig. 4b and, at higher magnification, 4c reveal, the shell contains pores. On the inner surface of these pores, crystallites can be observed. As EDX measurements confirm, the chemical composition of this shell type is very simple: the only metal present is calcium, i.e. the mineralised phases are calcite (as determined by X-ray diffraction) and possibly small amounts of $Ca(OH)_2$, portlandite. The presence of the latter phase can explain the evolution of water at comparably high temperatures. The textural features, i.e. the pores, can also explain the tendency of the samples to decrepitate, when the water vapor pressure in these pores rises to critical values.

Detailed EDX investigations on the eggshell from Hubei, China (Figs 5a and 5b), i.e. the amargasaurus sample, prove that crystallites of calcite (up to 80 µm diameter) are embedded in a microcrystalline quartz matrix.

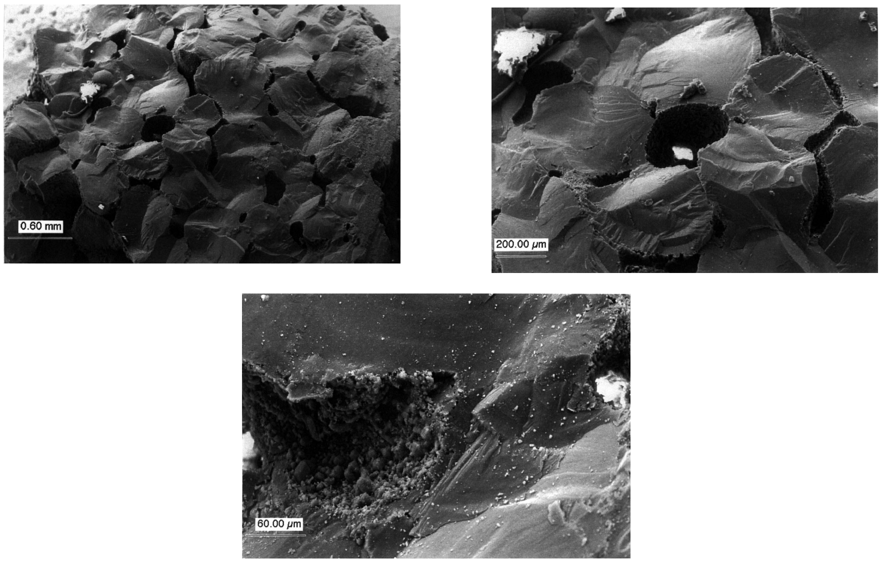

Fig. 4 Scanning electron micrographs of a fragment of the eggshell of a saltasaur (Salta, Argentina). As can be seen, the shells contain pores (b). On the inner surface of these pores, well-developed crystallites can be seen. EDX measurements reveal, that there are only calcium compounds present, i.e. calcite and, most probably, small amounts of portlandite

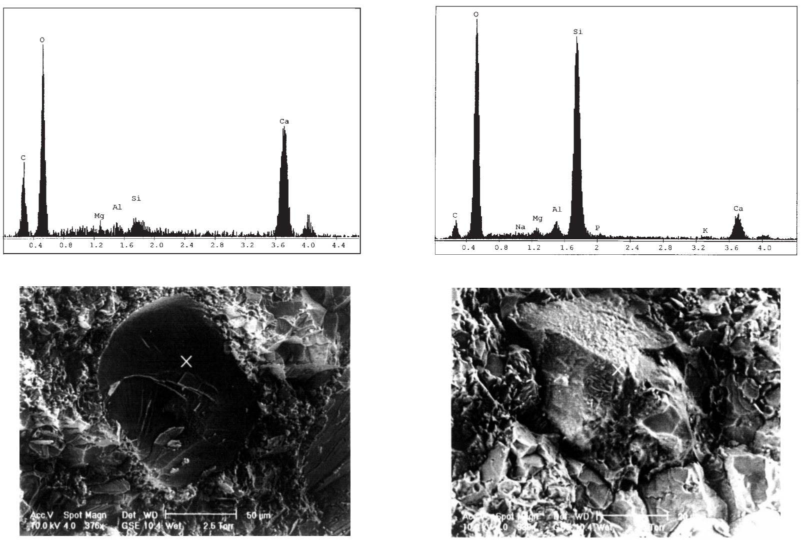

Fig. 5 Scanning electron micrographs and EDX measurements of a fragment of the eggshell of a amargasaur (Hubei, China) confirming the phase composition, i.e. the presence of calcite (a) and silica (b) microcrystals

Comparative thermogravimetric/mass spectrometric measurements (presented in Fig. 6a–c) gave evidence, that the registered mass losses allow a differentiation of the samples. In order to obtain reasonable thermogravimetric curves, all samples had to be crushed in an agate mortar. If not, decrepitations were always registered at temperatures around 400°C, and fragments of the samples were tossed out of the crucible. This observation is known from the thermal reactivity of geogenic materials containing gaseous and fluid inclusions. At increased temperatures, the vapor pressure of such inclusions reaches a level where the dense solid matrix decrepitates. In the case of finely dispersed material, these effects can be suppressed. Therefore, finely ground eggshell powders could be measured and evaluated quantitatively.

In general, two-step degradations are registered. The first step occurs in the temperature range near 400°C. The mass spectrometric investigations confirm that only water is evolved. The fact that this dehydration takes place at this rather high temperature can be explained by two factors: first, the evolved water is the product of the condensation of hydroxyl groups, which in turn, most probably, are constituents of

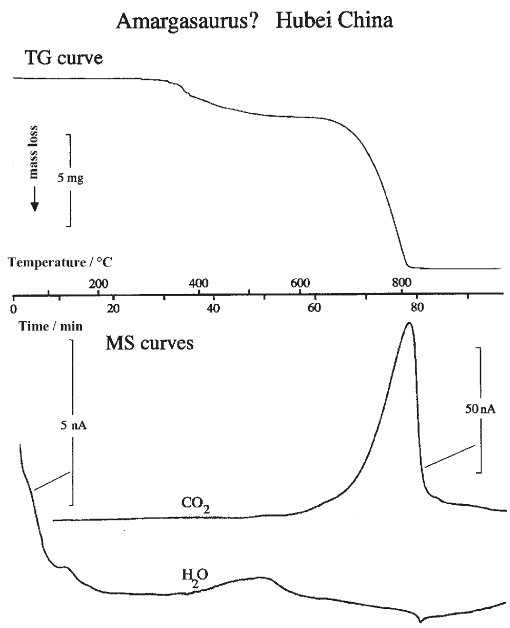

Fig. 6 Comparative thermogravimetric/mass spectrometric measurements of the thermal reactivity of fragments of dinosaur eggshells stemming from China, France and Argentina. The samples have been placed in platinum crucibles, and heated in air at 10°C min^{-1}
(a) Evaluation of the TG-MS measurement of the amargasaur eggshell reveals that the first mass loss (around 400°C) of 7.6% corresponds to the evolution of water, the second mass loss of 35.7%, which starts around 700°C, corresponds to the decomposition of calcite, i.e. CO_2 is evolved

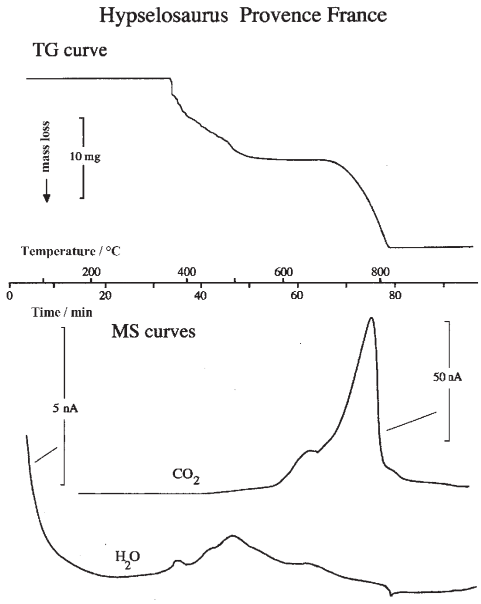

Fig. 6 (b) Evaluation of the TG-MS measurement of the hypselosaur eggshell also gives evidence for a two-step degradation. Again the loss of water (29%) in the first step and CO_2 (31.9%) are registered. The shape of the second step indicates the presence of dolomite: the process starts earlier than the one for calcite, which is characteristic for the decomposition of this mixed carbonate

nanocrystalline portlandite, $Ca(OH)_2$; second, these hydroxides are embedded in a calcite/silica/silicate matrix, which hinders the free evolution of volatile products and – in extreme cases – leads to the observed decrepitations. Although the sample had been pulverized by extended grinding, the thermogravimetric curve of the hypselosaur eggshell (Provence, France) still shows in the first degradation step (i.e. the loss of water), this phenomenon by its noisy, erratic course.

The mass losses in the temperature range above 650°C can be attributed to the decomposition of calcite, which has also been identified by X-ray diffraction. In the curves registered for the decomposition of hypselosaur (Fig. 6b) and saltasaur eggshells (Fig. 6c) small mass losses are observed before the main mass change occurs. Together with the mass spectroscopic identification of carbon dioxide as the volatile product, and with the chemical analysis, one can conclude that small amounts of dolomite may be present in these two samples. From the relative amounts of the volatile products one can also conclude that the samples contain different calcite/other phase ratios. In summary, the thermogravimetric/mass spectrometric measurements are strongly differentiating, but one has to take into account that the geochemical processes transforming the biogenic eggshell into a fossil mineral depend on the locali-

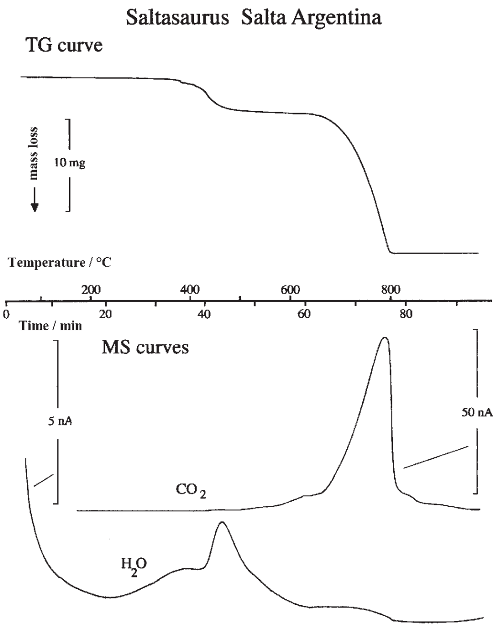

Fig. 6 (c) Evaluation of the TG-MS measurement of the saltasaur eggshell confirms partly the findings made for the two-step degradation of the hypselosaur specimens. Again the loss of water (9.3%) in the first step and CO_2 (40.9%) in the second step are registered. The shape of the second step indicates again that the specimen contains small amounts of dolomite

ties. Therefore, a large amount of further specific data has to be accumulated in order to build up comparable typologies.

Conclusions

In the best case, the study of biogenic and geogenic materials allows the reconstruction of historic facts and processes. However, specific insights into prehistoric periods allows the correlation of experimental data stemming from different complementary disciplines. In the case of petrified biogenic specimens, i.e. eggshells of different dinosaur species, mere phase analysis is insufficient. Morphological and textural features are very useful indicators for their specification and typologization. A typology (e.g. [5]), however, can only be developed if a critical amount of specific shell fragments with comparable construction schemes are known. Fortunately the past two decades were very productive with respect to accessible sites, where excavations could be carried out.

For petrified or fossilized materials, knowledge of the 'suffered' geochemical transformations is indispensable. As has been attempted in this report, complementary investigations of composition, structure, morphology, texture and thermal reactivity may yield essential results and, therefore, valuable mosaic stones for the reconstruction of historic events. Conclusive descriptions demand a much broader data base and are, by far, not yet available. But we hope to have shown that the specification of dinosaur eggshells by combined thermoanalytical and solid state chemical measurements is possible. There are still many, many specimens waiting to be characterized and typified. The goal for continuing is obvious: the improvement of our knowledge of this family of fascinating animals, and also for our endeavors to understand extremely slow geochemical processes.

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