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FOSSIL AGE DETERMINATION BY THERMAL ANALYSIS

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Subsequent to a comparative examination of recent bone material the author has recently completed the paleobiogeochemical evaluation of classical Quaternary and Pliocene terrestrial fossils of vertebrata from Hungary. A derivatograph (MOM) has been used to determine two thermoanalytical parameters which are closely associated with the passage of geological time: the total bound organic-matter content of the fossil and the fossilization coefficient.

Derivatographic measurement of the organic matter in the bones is supplemented by fine-structure analysis of bone-tissue slides.

Sample material of unknown age from several provenances was evaluated with the new dating method. The importance of the procedure is even greater in cases when only indefinite sporadic finds can be obtained from the sediments.

The geological dating of sedimentary rocks is one of the important problems of geological research. One reason for this is the inadequacy of the isotopic methods elaborated for the dating of magmatic rocks; more exactly, they are only suitable for the examination of certain, particular sediments. Thus, for example, the $K^{40}-Ar^{40}$ method can only be applied in the determination of glauconite-containing maritime formations.

The most widespread method for dating terrestrial sedimentary rocks is, at present, the C^{14} procedure. In addition to a number of possibilities of methodological error, its greatest deficiency is that it can be applied only in a geologically very narrow time interval of 60 000 years.

Another problem is that the isotopic methods and the recently elaborated dating procedures (magnetostratigraphy, racemic-aspartic acid method) demand special laboratory equipment and a large outlay, and hence are far from being widespread; in fact we might say that they are virtually lacking from current research work.

Thus, all endeavours are justified that have the aim of elaborating an up-to-date chronological method suitable for wide application in the geological laboratory.

The thermoanalytical dating method presented in this paper has been elaborated in the course of 15 years of paleobiogeochemical research [1]. Its basis is the correlative study of the temporal changes, the diagenesis of sedimentary rocks and the fossilization process, and the recognition of the phenomenon that the inorganic and organic chemical composition and structure of the fossils regularly change in a given geological environment as a function of time.

As regards their material composition, fossils can be grouped into two large categories. One is the carbonate-conchiolin system of lower-degree phyla, and the other is the apatite-collagen system of vertebrates. We have been concerned in more detail with the latter, with the examination of tooth and bone material, since our primary aim was the dating of terrestrial layers.

We have examined a number of methodological possibilities, of which the thermoanalytical method based on derivatographic measurements has proved the most suitable for tracing the changes in composition of bone material [2].

The underlying scientific basis for the selection of our particular sample material was provided by the comprehensive study of a French paleontologist Jean Chaline, who in a survey of the results of international research reviewed the chronostratigraphy of the classical Eurasian vertebrate localities [3]. The essential basis of the biochronological classification, which was calibrated with the absolute chronological data, was provided by the material of finds revealed in the karstic region of Hungary [4, 5].

Experimental

In the course of our work this chronologically well-defined sample material was evaluated, i.e. we performed comparative studies on vertebral segments of Ophidia indeterminata from the identical reddish-brown terra rossa of 14 karstic caves and crevices.

Since the total fine stratigraphic analysis of each locality was performed in our evaluation the data from hundreds of measurements were processed.

The derivatographic measurements were preceded by careful preparative work, the individual particular steps being: removal of the embedding sediment, grinding to indentical particle size, and removal of adsorptive water in an desiccator.

After examination of a number of methodological possibilities [6, 7], the series of measurements were performed under the following conditions: temperature range 1000°; rate of heating: 10°/minute in an air current; sample holder: platinum plate; sample weight: 200 – 300 mg.

Result and discussion

The thermoanalytical curves reveal processes of thermal decomposition shown in Fig. 1.

In the first, endothermic process the organic marcomolecules decompose and the water weakly-bound to the phosphate structure is lost.

During the second, exothermic process all the organic material burns and is removed, this oxidation being catalyzed by the platinum sample holder.

The collagen macromolecules also undergo deamination and decarboxylation. In parallel with the loss of the organic matter, the water strongly-bound to the phosphate structure is evolved continuously.

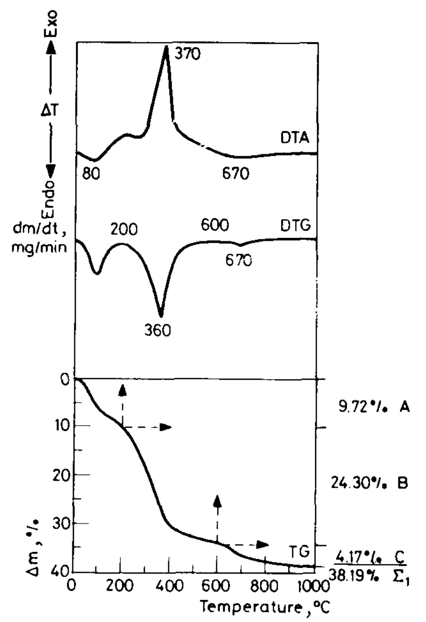

Fig. 1. Thermal curves of a Ophidia indeterminata vertebra segment in air atmosphere
A, *B*, *C* = thermodecomposition products

The third, endothermic process comes about only in the case of bone material older than 5000 years, and not in recent or prefossil samples. Here the inorganic carbonates secondarily built into the apatite structure dissociate an CO_2 is released. The loss of water bound to the apatite structure continues in this temperature range, too.

The percentage weight changes in the three well distinguishable stages are denoted by *A*, *B* and *C* respectively.

The great number of measured data demonstrated that the *B* and $A + B$ values decrease as a function of the embedding time. This trend is manifested in the relationship of the overlying layers of a given locality and of localities far away from one another. At the same time the value of *C* increases. Thus, the organic matter content of the bone material gradually decreases with the passage of time, in parallel with the gradual dehydration and carbonation of the apatite phosphate system. This finding was verified by supplementary research methods.

Figure 2 presents the fine-stratigraphical evaluation of the bone material collected in the sediment of the karstic crevice called Rigó-lyuk. It can be seen that the trend of the time-dependent changes in the derivatographically determined value of *B* agrees with that for the changes in nitrogen content determined by neutron activation analysis. This experiment justifies our conclusion that the thermal decomposition products removed during the first two thermal reactions are closely connected with the organic matter content of the bone. On the other hand, the

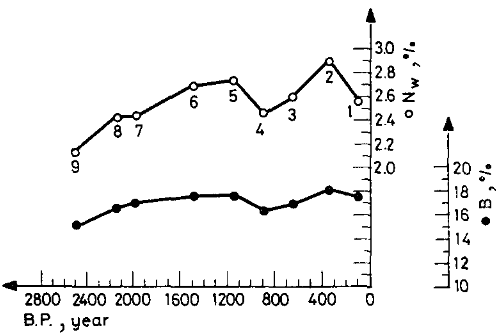

Fig. 2. The trend of time-dependent changes in the derivatographically determined *B*-value checked by neutron activation analysis

Figure demonstrates the decrease in the organic material parallel with embedding. The continuous trend is interrupted by two minima. This is a very important interpretable phenomenon. Evaluation of the rock and the embedded material of the finds shows that in these time intervals the prevailing climate was warm and humid in these regions. As a result of enhanced microbiological decomposition the organic matter content of the bones is lower than the average. The minimum organic matter contents assigned to the two points of time appeared consistently in the fine-stratigraphic evaluation of more than one locality, proving the informative usefulness of the derivatographic parameters in paleoclimatological reconstructions.

For a more exact interpretation of the termal decomposition, the series of derivatographic measurements were supplemented by several gas titrimetric examinations.

In Figs 3 and 4 the results of gas titrimetric examinations of vertebral segments (a fragment of 6500 years and another fragment of 1 000 000 years) are presented. The measurements were made in nitrogen atmosphere, the aim being the determination of the CO_2 content.

The DTA curve plotted in air atmosphere is also given.

On heating in the inert atmosphere the release of CO_2 begins at 250°. The first stage of gas release is obviously the effect of decarboxylation of the collagen while in the higher temperature range the inorganic carbonates (calcite, magnesito-calcite) dissociate.

The pH or the adsorber solution shifts in the alkaline direction until the complete release of CO_2 showing that, in addition to water, ammonia is produced, by deamination.

The two thermal curves together with the gas titrimetry results reveal that the organic matter content of the younger sample is essentially higher, while its inorganic carbonate content is lower.

The changes in inorganic-organic composition are similarly demonstrated by the structural picture of the transverse sections of the two vertebral segments

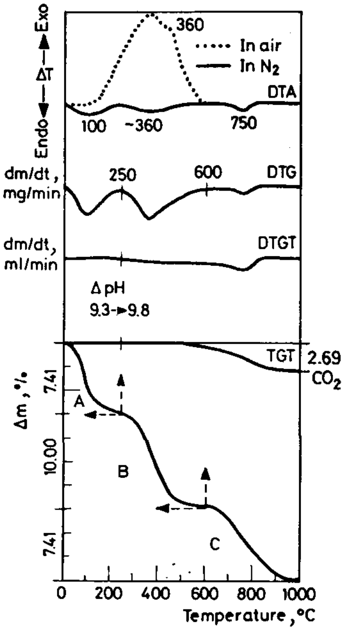

Fig. 3. Thermogas titrimetric examination of a 6500-year-old vertebra segment

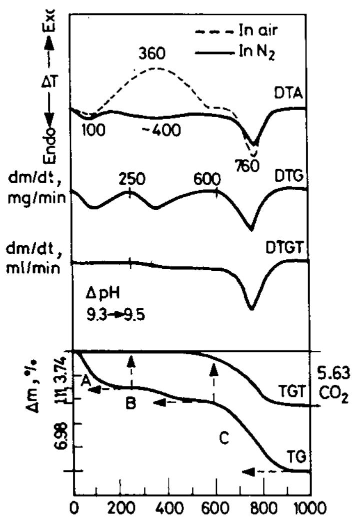

Fig. 4. Thermogas titrimetric examination of a 1 000 000-year-old vertebra segment

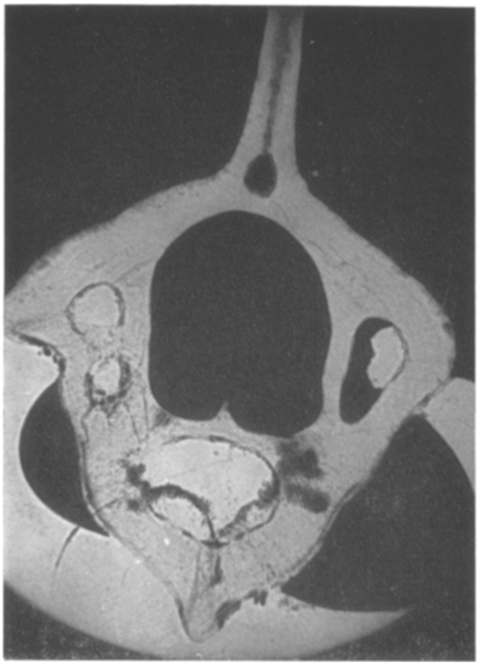

Fig. 5. The tissue of the Holocene vertebral material

(Figs 5–6). The tissue of the Holocene vertebral material is intact and is totally indentical with the structure of a recent sample, whereas in the case of the Pleistocene vertebra some smaller or larger resorbed cavities can be observed.

The trends of the fossilization process can be summarized by means of our derivatographic parameters. In addition to the value $A + B$ relating to the organic matter content, the fossilization coefficient (denoted by F_k) was introduced, this being the quotient of the values $A + B$ and C.

The large number of data from the serial derivatographic measurements were processed by computer. The parameters $A + B$ and F_K were correlated with the absolute time values of Chaline's biochronological table. The exponential, logarithmic and power-form regression trend calculations were performed separately for the Holocene, Pleistocene and Pliocene periods and it was established that the regression coefficients of the latter two provide applicable numerical correlations.

The correlation lines established for the Holocene and the correlations for the individual geological periods are presented is Fig. 7 and Table 1.

Subsequently, the derivatographic time data of finds of unknown age were determined (Table 2). Two of the data in the Table were checked with C^{14} dating. The validity of our dating seems to be supported in the case of the other values too, since they are completely consistent with the stratigraphic determinations, with the relative chronological order based on the changes in vertebrate succession.

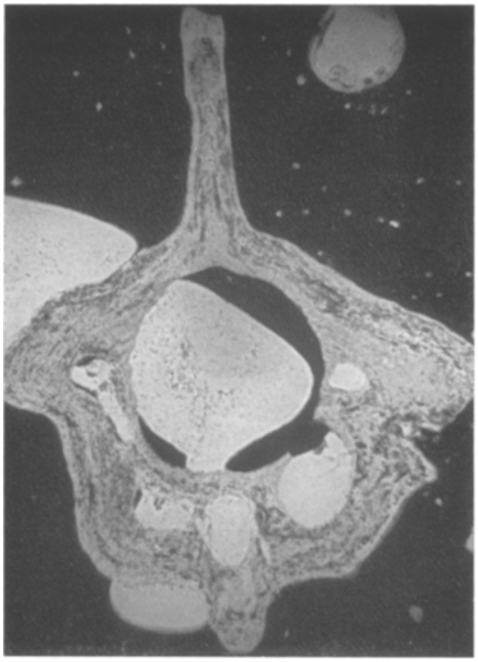

Fig. 6. The tissue of the Pleistocene vertebral material

Table 1

The correlation for the individual geological periods

Holocene	Pleistocene	Pliocene
$Fk > 4.0; (A+B) > 28.1\%$	$2.0 < Fk < 4.0; 11.0\% < (A+B) < 23.6\%$	$Fk < 1.0; (A+B) < 7.0\%$
$T_{abs.} = 10^2 \cdot e^{-\frac{(A+B)-29.71}{1.29}}$	$T_{abs.} = 10^3 \cdot \left(\frac{28.483}{(A+B)}\right)^{5,3124}$	$T_{abs.} = 10^3 \left(\frac{28.483}{(A+B)}\right)^{5,3124}$
$Fk > 4.0; 23.6\% < (A+B) < 28.1\%$	$Fk > 4.0; 11.0\% < (A+B) < 23.6\%$	
$T_{abs.} = 10^2 \cdot e^{-\frac{(A+B)-30.63}{1.78}}$	$T_{abs.} = 10^3 \cdot e^{-\frac{(A+B)-33.86}{2.60}}$	
$Fk > 4.0; (A+B) < 23.6\%$	$Fk < 2.0; 7.0 < (A+B) < 11.0\%$	$T_{abs.}$ = B. P. Years
$T_{abs.} = 10^2 \cdot e_{-}\frac{(A+B)-33.86}{2.60}$	$T_{abs.} = 10^3 \cdot \left(\frac{28.483}{(A+B)}\right)^{5,3124}$	$Fk(A+B)$ = derivatographical parameters

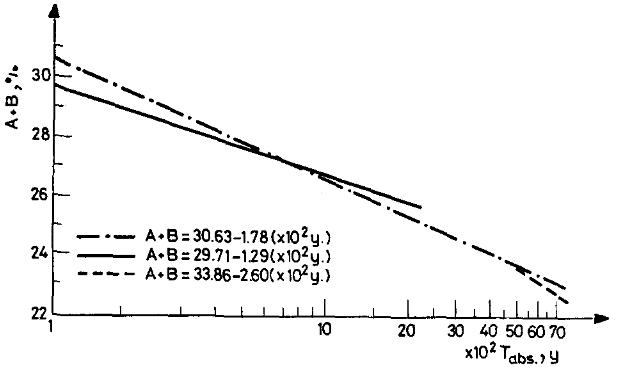

Fig. 7. The correlation lines established for the Holocene

Table 2

The new derivatographic time data

Localities (caves)	Periods	Faunal phases	Derivatographical ages (B.P. years)
Csontos	Holocene	Alföldi	15 (recent)
Békásmegyer		Bükki	3 897 (±250)
Baradla		Körösi	*6 516 (±250)
Zöld		Körösi	7 314 (±250)
Balla	Pleistocene	Istállóskői	*20 040 (±500)
Por-lyuk		Varbói	36 786 (±500)
Osztramos-4		Upponyi	259 981 (±5000)
Osztramos-5		Templomhegyi	347 200 (±5000)
Osztramos-14		Betfiai	695 109 (±10 000)
Osztramos-12		Betfiai	979 800 (±10 000)
Osztramos-13	Pliocene	Estramontiai	3 077 942 (±100 000)

* = Checked by C^{14}-method

Work is continuing on the further development of the method to make it suitable for the evaluation of the sample material other sedimentary rock facies, such as loess. Thus, the series of experiments performed on the bone material will be extended to the conchiolin-carbonate biomineralized system of molluscs.

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ZUSAMMENFASSUNG — Nach einer vergleichenden Untersuchung an neuzeitlichem Knochenmaterial hat der Autor kürzlich die paleobiogeochemische Auswertung der klassischen Quaternären und Pliocenen terrestren Fossilien von Vertebraten aus Ungarn ergänzt.

Ein Derivatograph (MOM) wurde zur Bestimmung zweier thermoanalytischer Parameter eingesetzt, die eng mit dem Fortschreiten der geologischen Zeit verbunden waren: dem Gesamtgehalt an gebundenem organischem Material und dem Fossilisationskoeffizienten.

Die derivatographische Messung der organischen Substanz in den Knochen wurde durch die Feinstrukturanalyse von Knochengewebeschnitten ergänzt.

Probenmaterial unbekannten Alters verschiedener Herkunft wurde mit der neuen Methode ausgewertet. Die Bedeutung des Verfahrens ist in den Fällen noch grösser, wenn aus den Sedimenten nur unbestimmte sporadische Funde erhalten werden können.

Резюме — После сравнительного исследования нового костного материала, автор недавно провел палеобиогеохимическую оценку земных окаменелостей позвоночных четвертичного и плиоценового периода. Дериватограф (МОМ) был использован для определения двух термоаналитических параметров, которые тесно связаны с прохождением геологического времени: общее количество связанного органического вещества окаменелостей и коэффициент окаменелости. Дериватографическое измерение органического вещества в костях дополнено тонко-структурным анализом образцов костной ткани. Образец материала неизвестного возраста был установлен с помощью этого нового метода датирования. Значение этого метода даже больше в тех случаях, когда только неореinternalленные спорадические находки найдены в геологических отложениях .