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SEDIMENTAL CORRELATIONS. A POSSIBILITY FOR THE DETERMINATION OF RELATIVE CHRONOLOGY ON THE BASIS OF THE THERMOANALYTIC (DERIVATOGRAPHIC) INVESTIGATION OF THE ORGANIC MATERIAL CONTENT OF FOSSILS

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ABSTRACT

The aim of the study is to propound a conceptional consideration and to call attention to the results of paleobiochemical investigations, which allow to draw the conclusion that a new procedure can be elaborated for geological epoch determinations. This statement applies to sediments embedding persistent taxons, and is valid within the limit of 30—35 million years. The author considers as taxon specific the molluscan shell and mammalian bones (fossil remainders) as an organic calcified biogenic system, in its entirety. Contrary to previous methods, comparisons of the bones and shells from different geological epochs were performed by the thermoanalytic (derivatographic) measurement of the total amount of so-called bound water and organic material.

PRESENTATION OF THE PROBLEM

The objective of the present study is to describe an assumption, and to call attention to a possibility for the elaboration of a new method that might enable us to trace the passage of geological time, or to perform the correlation of sediments that include only persistent taxons. The assumption is based on the fact that, under favourable conditions of fossilization, the conchiolin and collagen contained in molluscan shells and vertebrate bones decompose, in the geological sense, very slowly, following a well-defined law. Detailed studies on this kind of decomposition have been done in the recent past, the process was described in detail and summarized by DEGENS [1967]. The schematic decomposition process is as follows:

The initial fast aerobic decomposition of the outer soft parts is followed by the slow autohydrolysis of the organic matter contained in the shell, the end product being "free" amino acid in solvent phase or "bound" amino acid, peptide-bound, or forming metal complexes. Fossilization is completed by the dissolution of the inorganic matter of the shell, or by silica gel saturation, and recrystallization. In the course of this process, the amino acid is solved out, gets bound in the environment, or decomposes through deamination, decarboxylation. The question is whether or not the gradual decomposition of the organic matter included in the shell can be traced. Results obtained from paleobiological investigations give a positive answer. The stepwise decomposition of conchiolin has been verified by ABELSON [1955] and HARE [1966] through the estimation of the amino acid content of the molluscan shell, by TONG YUN-HO [1966] through the comparison of "shell protein—nitrogen content". GREGOIRE [1966, 1968, 1970, 1972] analysed, by electron-microscopic techniques, the shell protein of Cephalopoda, and cleared up, in detail, the diagenetic and thermometamorphic effects, at the same time theoretically verifying temporal graduality. SZÖŐR [1969, 1971*a*, 1972*a*, *b*] traced the organic matter content of the Bivalvia shell, gave a sketch of the possibility of taxonomic identification by the so-called derivatographic fingerprints, for the sake of fragmentary material identification, as well as for facies indication and convergence determination. During his studies the latter author observed that, in the case of Bivalvial fossils enclosed in identical environment, with similar paleoecological background and exposed to solid fossilization effects (*i.e.* no recrystallization, no dissolution, no thermometamorphism), the organic material content of the shells gradually decreases with the passage of time. Naturally, the results refer to persistent taxons, to taxons displaying identical shell structures, and to comparison within one genus. The regularity was observed up to the Miocene Era inclusive, whereas the investigation of mesozoic Bivalvia shells yielded no evaluable data. The aim of the present study is to report on the results of investigations so far performed and extended to vertebrate bones and gastropod shells, as well as to sum up the results so far obtained for the Bivalvia group.

MATERIALS AND METHODS

The investigations were performed on Ophidia vertebrae, from the taxonomic category of Vertebrata, collected in karstic caves in Hungary. The geological and speleological determination of the localities has been partly completed, or is under way. The localities Bodajk and Villány-6 were reported on by Kretzoi [1956, 1964], the localities Csontos-, Vár-, Zöld caves by Kordos [1969, 1970, 1972], the locality Porlyuk by Jánossy *et. al.* [1972]. During the analysis 64 vertebrate segments were investigated by the dresent author (the samples were obtained from Kordos). From the group Gastropoda the taxons *Cepaea* and *Planorbarius* were analysed, the samples and locality references were placed at the present author's disposal and characterized by Krolopp [in Bartha, 1971]. Examinations were performed on 47 shells.

The Bivalvia group (the genera *Arca, Avicula, Pinna, Mytilus, Ostrea, Cardium, Venus, Tellina, Lucina, Glycimeris, Cardita* and *Donax* altogether 380 shells, were studied in previous years by Szöőr [1969, 1972*a*], and detailed description of the results was given together with the data of the localities.

The sample preparation methods and the data obtained wiht the MOM type derivatograph were given account of in previous publications [Szöőr, 1969, 1971*b*, 1972*a*]. In the present study the essential problem is the weight per cent comparison of the materials removed by heating. Thus, in the derivatograms published here *(Figs. 1, 2, 3)* only the typical changes of the DTG-, TG curves are presented. The data of the TG curve are summarized in detail in Tables 1, 2, 3.

RESULTS

a) Investigation of Ophidia vertebrae

It is obvious from both Table 1, which summarizes the results, and from *Fig. 1,* which compares some derivatograms demonstrating the changes due to thermal effect, that the thermal losses taking place in the course of thermal analysis are as follows:

A = loss of water weakly bound to organic and mineral structures, endothermal process

B = loss of organic matter, exothermic process

C = release of carbon dioxide, due to the decomposition of the carbonate apatite structure, endothermic process

D = water released from clay minerals, endothermic process

Σ_1 = total loss of material, and Σ_2 = residue after heating.

TABLE I

Derivatographic analysis of Ophidia vertebrae, thermogravimetric /TG/ conditions

Sample	Number of analyses	Age	Weight per cent values of the TG curve					
			A	B	C	D	1	2
Museological sample	2	recent	13.14	39.20	4.07	—	65.41	43.59
Zöld cave, 2 strata, Pilis Mountains	6	Holocene	7.50	15.20	3.80	—	26.50	73.50
Csontos cave, Oszoly	8	Holocene	8.80	23.40	2.52	—	34.72	65.28
Kőköz, crevice accretion, 4 strata Felsőtárkány	12	Pleistocene, Würm	6.43	7.38	7.86	—	21.67	78.33
Kőköz, crevice accretion, 1 stratum Felsőtárkány	6	Pleistocene, Riss-Würm	6.22	5.28	4.11	1.28	16.89	83.11
Kőköz, crevice accretion, 2 strata Felsőtárkány	4	Pleistocene, Riss-Würm	7.04	3.64	4.09	1.59	16.36	83.64
Porlyuk ditch, 2 strata, Jósvafő	8	Pleistocene, Riss-Würm	7.80	10.70	3.40	—	21.90	78.10
Vár cave, Budapest	6	Pleistocene, Mindel	5.02	4.35	7.02	—	16.39	83.61
Villány-6, crevice accretion, Villány Mountains	2	Pleistocene, Mindel	6.74	2.61	3.80	2.61	14.02	85.98
Bodajk, crevice accretion, Vértes Mountains	6	Middle Oligocene	4.96	2.38	3.51	1.86	12.71	87.29

A = water bound to organic and mineral structure,
B = organic matter
C = CO_2 released from carbonate apatite, D = water bound to clay minerals
1 = total loss of material, 2 = residue after heating

It is striking that the organic matter content gradually decreases depending on the length of the period of embedding. Inconstistent with this trend is the sample material from two strata of Porlyuk ditch with the high value of 10.70 %. With the other forms of material loss, *i.e.* loss of water, release of carbon dioxide, total loss of material and residue after heating no such correlation can be observed. It is noteworthy that on the samples collected from several localities clay mineral formation can be observed. The clay mineral, in our opinion, is no structural component of the bone material, but an impurity filling up the cracks. Very naturally, in this case, in connection with the loss of water (denoted by A), the release of OH bound to clay mineral must also be taken into account.

b) Investigation of Gastropod shells

It was also observed in the study on gastropod shells, in consistence with the previous results form studies on Bivalvia shells that if embedding is young, a taxonomic difference can be pointed out (derivatographic fingerprint up to the level of genus, SZÖŐR, 1972*a*). The derivatographic image (fingerprint) of the genus Planorbarius differs noticeably in the given geological time interval. During the study of the species Planorbarius, material losses A, B and C were observed, whereas the species

Cepaea considerably differs by the occurrence of the material loss O. The results are summarized in Tables 2 and 3, and illustrated in *Figs. 2* and *3*. In the Figures only the thermal reactions up to 700 °C are presented, since great-scale release of carbon dioxide (C) can only be measured by another way of programming. Consistent with

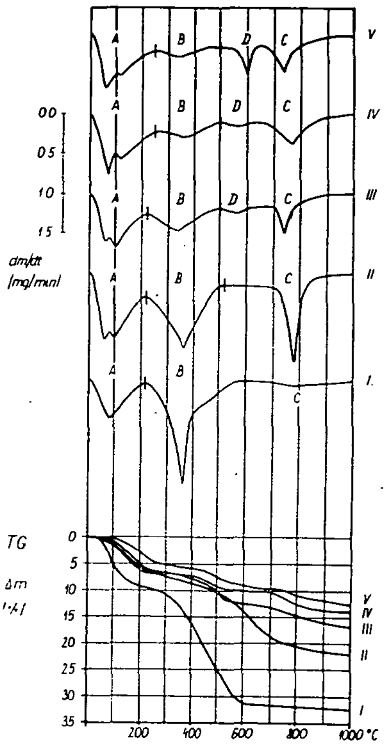

Fig. 1. Derivato-thermogravimetric (DTG) and thermogravimetric (TG) analysis of *Ophidia* vertebrae

I = Holocene (Oszoly), II = Pleistocene, Würm (Felsőtárkány), III = Pleistocene, Riss-Würm (Felsőtárkány), IV = Pleistocene, Mindel (Villány-6), V = Middle Oligocene (Bodajk), A = release of water bound to organic and mineral structure (endothermic) B = release of organic matter (exothermic), C = release of carbon dioxide from the carbonate-apatite structure (endothermic), D = release of water bound to clay mineral (endothermic)

those previously described is the interpretation of columns A and B, the C values denote the amount of carbon dioxide released from calcium carbonate. The material loss denoted by O has not yet been exactly defined, it may consist either in the loss of water enclosed in the aragonite structure [Hudson, 1967] or in the burn-out of organic matter or perhaps the sum of both. Burn-out of organic matter is the easiest to prove. It is well-known that in the shell of the species Cepaea a pattern built up of organic material can be seen. A similar material loss was observed during the examination of the species Neritina, the shell of which similarly displays some pattern [Szöőr, 1971*a*]. The DTA curve (not shown in the Figure) also indicates a slight exothermic slope. This is why in the Table the value O is assigned to the value B, and the amount of organic matter is compared with the value B+O.

TABLE 2

Derivatographic analysis of shells of the species Planorbarius, thermogravimetric /TG/ conditions

Sample	Number of analyses	Age	Weight per cent values for the TG curve				
			A	B	C	Σ_1	Σ_2
Planorbarius corneus (L), Bratislava	6	recent	0.4545	2.3636	40.8183	43.6364	56.3636
Planorbarius corneus (L), Sárrét	6	Holocene	0.4546	1.3182	40.9545	42.7273	57.2727
Planorbarius corneus (L), Tószeg	4	Pleistocene	0.4009	0.8726	40.2359	41.5094	58.4906
sp. *Planorbarius*, Várpalota	5	Upper Pannonian	0.3846	0.7692	40.2247	41.3785	58.6215
Planorbarius cornu manteli, (DUNK) Öcs	7	Upper Pannonian	0.3714	0.7749	40.2113	41.3576	58.6424

A = water bound to organic and mineral structure
B = organic matter
C = CO_2 released from calcium carbonate
Σ_1 = total loss of material
Σ_2 = residue after heating

With both species the amount of organic matter (sp. Planorbarius in Table 2, column B; sp. Cepaea — Table 3, column B+O) gradually decreases depending on the length of the embedding period. Such a correlation cannot be established by measuring the amount of released water or carbonate. Unlike the case of Ophidia vertebrae, the total loss of material (Σ_1), and residue of heating (Σ_2) values — inversely proportional to each other — are in correlation with the period of embedding.

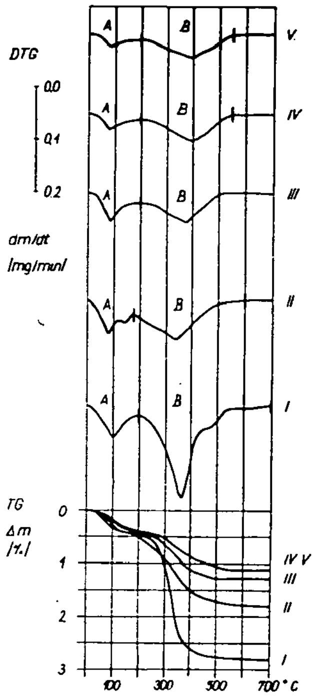

Fig. 2. Derivato-thermogravimetric (DTG) and thermogravimetric (TG) analysis of several species of *Planorbarius*
I = Recent (Bratislava), II = Holocene (Sárrét) III = Pleistocene (Tószeg), IV, V = Upper Pannonian (Öcs, Várpalota), A = release of water bound to organic and mineral structure (endothermic), B = release of organic matter (exothermic)

SUMMARY OF RESULTS. CONCLUSIONS

All that have been described so far unequivocally prove that the amount of organic matter detectable in gastropod shells and vertebrate bones gradually decreases with the passage of geological time. This statement is supported by a similar conclusion drawn previously in connection with Bivalvia shells. *Fig. 4* serves to demonstrate this regularity. Here the organic matter content of the shells or bones of the taxonomic groups under study (weight per cent values) is compared with the geological age and the period of embedding.

The curve referring to Bivalvia shells, naturally, is interpreted in a global way, since it sums up the mean values for a number of genera. In this sense, it characterizes only the fossilization, the stepwise organic matter loss of the marine, littoral-sub-

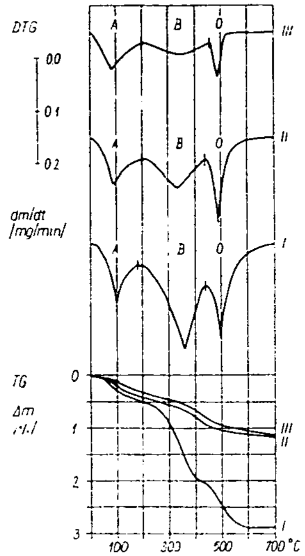

Fig. 3. Derivato-gravimetric (DTG) and thermogravimetric (TG) analysis of several species of *Cepaea*
I = Recent (museological sample), II = Pleistocene, Mindel (Vértesszőlős), III = Miocene (Mainz), A = release of water bound to organic and mineral structure (endothermic), B and O = loss and burn-out of organic matter in two steps (exothermic)

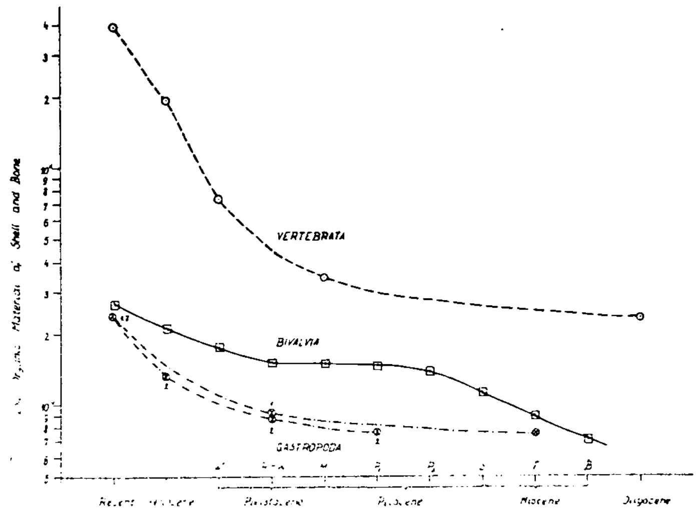

Fig. 4. Loss of organic matter in vertebrate bones, gastropod and Bivalvia shells depending on embedding time
Vertebrata = Ophidia vertebrae (64 samples), *Bivalvia* = genera: Arca, Avicula, Pinna, Mytilus, Ostrea, Cardium, Venus, Tellina, Lucina, Cardita, Donax (380 samples), *Gastropoda* = 1) genus Cepaea, 2) genus Planorbarius (47 samples), W = Würm, R—W = Riss—Würm, M = Mindel, P_1 = Upper Pliocene, P_2 = Lower Pliocene, S = Sarmatian, T = Tortonian, B = Burdigalian

TABLE 3

Derivatographic investigation of shells of sp. Cepaea, thermogravimetric /TG/ conditions

Sample	No. of analyses	Age	Weight per cent values of the TG curve						
			A	B	O	B+O	C	Σ_1	Σ_2
Cepaea vindobonensis (FÉR.), museological sample	6	Recent	0.4893	1.5902	0.7951	2.3853	41.7737	44.6483	55.3517
Cepaea vindobonensis (FÉR.), Vértesszőllős	6	Pleistocene	0.2602	0.5004	0.4003	0.9007	42.0737	43.2346	56.7654
Cepaea subglobosa ( ), Mainz	6	Miocene	0.3670	0.5505	0.2294	0.7799	41.9723	43.1192	56.8808

A = water bound to organic and mineral structure
B and O release and burn-out of organic matter in two steps
C = CO_2 released from calcium carbonate
Σ_1 = total loss of material, Σ_2 = residue after heating

littoral biotope, shellfish population embedded in silty sand. It calls attention to the fact that there is a possibility for such a categorization and summarization in the case of a great number of sample materials.

The investigation on Ophidia vertebrae proves that the measurement as well as the comparison of organic matter through the derivatographic method can be performed also with bone material. This fact has been theoretically verified, with reference to historical periods, by Dávid [1969] and Kiszely [1969] through the derivatographic study of subfossil human bones. The apatite structure that builds up the bones contains significantly more organic matter than the calcite- and aragonite-containing shell. Even vertebra segments embedded in cave sediments from the Pliocene enclose more organic matter than recent molluscan shells (without the periostracum). It should be mentioned here that the similar examination of tooth material, in view of the extremely high resistance of the dental enamel, promises even more favourable results.

When describing the results, mention was made that the material from a single cave (Porlyuk ditch, 2 strata, Jósvafő) does not fit in with the trend of organic matter decrease. The organic matter content of 10.70%, denotes a much younger time of embedding (Holocene), instead of the present chronological assignment (Pleistocene, Riss-Würm). This facts sets us an objective to study the given formation in fuller detail.

The organic matter content of Cepaea and Planorbarius shells is even less than that of Bivalvia shells. The difference observed on corresponding recent species gets even more pronounced during fossilization. The thin shell of snails made up of aragonite gets more damaged than the thicker calcite and calcite-aragonite-containing shells of shellfish. In spite of this, the taxonomic specificity observable on the genus level can be established, and this gives a basis for chronological comparison.

To go back to the original concept, the essentials can be drawn up as follows:

The fossilization of shells, snail-horns, bones can be traced and graded. The residual organic matter content, as a well-defined measure, can characteristically reflect the passage of time. Such an assessment of time, very naturally, belongs in the field of relative chronology, but obviously can be applied to settle the given problem. Such problems may be the fine levelling, chronological description of a sedimental conglomerate, its correlation to the similar ones, which can be hardly or not at all performed either on the grounds of the properties of the lithofacies (uniform sedimental conglomerate), or the properties of the biofacies (persistent fauna). In such investigations the most essential requirement is that the comparison be performed within a given taxonomic group — in ideal cases on the genus level. Examinations can be performed only on fossil samples that have not been crystallized, imbued or exposed to metamorphic effects. If molluscan shells are available as fragment material (lumasella) — particularly when analysing samples from bores — the work begins with structural analysis by optical methods [Bøggild, 1930; Oberling, 1964; Taylor *et al.*, 1964, 1973]. Organic matter content is determined through the derivatographic measurement of the thus defined fragment materials of identical structure.

Furthemore, it can be expected that in the case of Holocene, Pleistocene, Pliocene fossils, on the grounds of the evaluation of a great number of samples, through the statistical evaluation of the results and organic matter measurement, an absolute chronology can be established.

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