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THE INSTRUMENTAL ANALYSIS OF MODERN VERTEBRATE TOOTH AS FOSSIL MODEL MATERIAL

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INTRODUCTION

The detailed biochemical instrumental analytical investigation of the Mollusca shell, as well as a similar interpretation of the taxonomic and fossilization problems directed attention to the thermoanalytical research of the biogenic calcified systems.

In recent years [SZÖŐR, 1969] in the course of the complex thermoanalytical investigations of the modern and fossil Mollusca shell by means of the Derivatograph apparatus [PAULIK *et al.*, 1958] — as "$CaCO_3$-konchiolin" inorganic-organic system — it was verified that a new investigational direction was devised which reflected taxon specificity and followed the line of fossilization processes.

In the course of the investigations it became obvious that the inorganic structure variations brought about by the specific protein, the quantity and ratio of the inorganic and organic components, manifest themselves perceptively, thereby determining the thermoanalytical processes. Thus, the DTA-, DTG-, and TG-relations, in conformity with modern species, reflect species-specific information, or, in the case of Pleistocene, Pliocene, and Tortonian fossils under favourable embedding conditions, reflect signals interpreting genetic specificity. The reproducible results obtained from the fossiliferous species ensured an identification possibility of the hardly evaluable fragmental material obtained from the sediment. The work of comparison took into account the diverse palaeocologic and fossilizational possibilities. Such a comparison of the samples of the diverse fossiliferous biotopes (facies) [SZÖŐR, 1970, 1971] offered new facies-indication possibilities of relying on absolute index numbers. The elaboration of this new research direction is still in progress, but we deemed it absolutely necessary to extend the investigations from the Mollusca group to the Vertebrate taxon. This endeavour was stimulated by our desire to get acquainted with the thermoanalytical properties of the "apatite-collagen" inorganic-organic biogen system. Furthermore, to establish whether we can obtain information about the modern Vertebrate species with the method elaborated in connection with the Mollusca shell, or by any other comparative systematic method, or — in the case of fossiliferous species — paleosystematic, facies-indicational information characteristic of fossilization. The results reported in this paper give an account of the experiences gained while elaborating the course of methodology to be followed in a series of experiments which will probably take a long time.

The vertebrate fossil material obtained in masses from the sedimentary rocks contains for the most part bones and teeth, only rarely do other components come to light, *i. e.* primarily scales of fishes, hides, hair formation, and it would certainly create a sensation to find again the carcass of a mammoth frozen in the ice, or a fossil either mummified or embedded in bitumen or fossil wax. The biochemical evaluation is of course confined to these "ideally" fossilized findings. KERNBACH [1924], BOYD et BOYD [1934, 1937], YAMADA [1934], GRAF [1949], as precursors determined albumins, the ABO blood group, and active lipase and histamine from human mummy material. STEPPUHN and LJUBOWCOWA [1930] made us acquainted with the active proteolitic enzyme of a mummy and mammoth. THIEME *et al.*, [1956] determined a blood group from a fragment of a human pleistocene skull. SINEX et FARIS [1959] examined the gelatine of the antlers of a 12000 year old stag, DROZDOWA [1962] the collagen of the scalp of a mummified amphibian from the Lower Permian. HELLER [1966] revealed the fossilizational differences of the diversified vertebrate material obtained from the Anisian and Ladinian bitumen shale, the Liasic Posidonomia shale, and from the Rancho La Brea asphalt pit, thereby verifying the preserving effect of the bitumen embedding. WYCOFF [1969] reported on the spectrum of protein amino acids isolated from the Dinosaurus bones of the Jurassic and Cretaceous period.

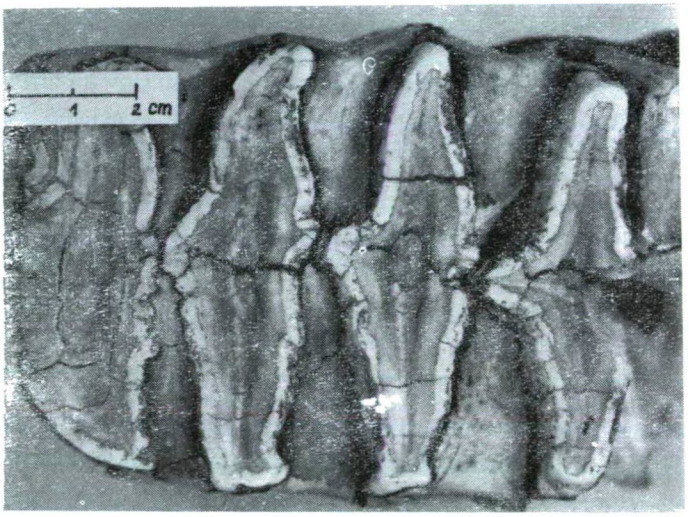

Fig. 1. Structures of the Loxodonta africana tooth. Top view, cement without, enamel in the middle, dentine within.

We attribute great importance to these results. On the one hand they prove that also the vertebrate remains have their specific proteinmaterial survival possibility, and that the subsisting organic material as indicator shows that the inorganic structures have not yet crystallized, have not yet been dissolved, but still preserve their original pattern. On the other hand they indirectly call attention to the fact that it is

worth while to go on investigating systematically the less "ideally" subsisting tooth and bone remains with similar or other methods. In general we chose the tooth material as object of our investigations, justifying our decision with the following reasons:

1) The great number of fossil teeth is, generally better preserved than the bone material, in the case of modern research material: a better "access" possibility.

2) The tooth reflects the evolutional, phylogenetic changes much more sensitively than the bone material, in this respect it is a morphologically well defined investigation material, and suitable for comparison.

3) The study of the taxonspecific, diversified structure assemblage brought about by the collagen of the tooth, a typical inorganic substance-building protein, has for a long time been an effective method for systematic problems [CHALINE, 1968].

4) The thermoanalytical research of the tooth as human material has already begun in our country [SIMON *et al.*, 1969. BERÉNYI *et al.*, 1970].

5) The crystallo-chemical aspects of the mineral components of the teeth (problem of dahllite and francolite) were investigated and analysed in detail a. o. MCCONELL [1938, 1952a, 1952b, 1960].

The present investigations were carried out on the lamellar molar of a recent African elephant (Loxodonta africana) obtained from the material of the museum of the Hungarian Geological Survey *(Fig. 1)*. The selection of the sample was justified by the following points of view: The objective of this work was to get to know which of the instrumental analytical methods employed by us would be the most suitable for revealing the physico-chemical differences of the structure units constructing the tooth. The available possibilities must be considered, and we must select the method or methods which seem to be the most appropriate, by means of which we at first compare modern species with one another, and then the tooth material of corresponding fossils. Since it is a question of elaborating several procedures, we needed a great deal of dentin, enamel, and cement which could be separated analytically. By means of its size and morphological structure the Loxodonta tooth meets these requirement in every respect. The selection was further justified by the fact that the Loxodonta tooth differs from the structure of many vertebrate taxon teeth by a structural unit, the presence of the cement layer. The chemical, physical investigation and evaluation of the cement layer, to the best of our knowledge, has not been performed as yet.

METHODS AND RESULTS

Preparation

The cement, enamel, and dentin layers were separated from each other mechanically. The larger pieces were prepared with a chisel and hammer, while the enamel was cut off the dentin with a dental diamond-disc under constant cooling. The thus obtained pieces were broken up and then ground in an agate grinding-mill (heating 1 h/1°C)below the grain-domain of 0,06 mm∅. The preparations were then stored in an air-tight glass vessel. An average of the material was taken for each examination.

Though my aim was the uniform investigation of the organic and inorganic totality, yet, for the sake of evaluation, I solved the separation of the organic assemblage (protein, lipid, mucoprotein, etc.) from the inorganic fraction (carbonate-oxyapatite) so that neither should be impaired. The organic fraction was prepared in the following way: the inorganic totality, dialysed in sterile environment, was carried

into solution (0,268 M (10%) EDTA; pH 7,4) at 5°C. The organic material remaining in the dialysis-membrane was collected and lyophilized and immediately utilized after treatment (IR-spectroscopy). The inorganic fraction was obtained by dissolving the organic material by constant strirring in a solution consisting of 0,5 *N* NaOH (carbonate-free) and glycerine over a water-bath, decanting the supernatant several times, washing it with distilled water, and drying it at room temperature (Derivatography).

Microscopic comparison

A thin section was prepared from the tooth at a depth of 1 cm from the surface, parallel to the axis of the tooth, and crossing the cement, enamel, and dentin layers obliquely. The structures were examined in two different ways. With the thin section

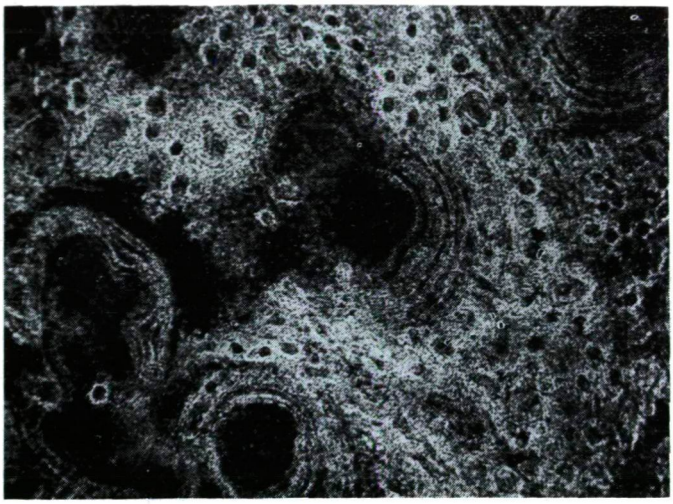

Fig. 2. A microscopic picture of cement in transmitted light, parallel nicols. Magn. 28:1.

method, in unpolarized light, the following phenomena can be observed: the cement layer is crystal-aggregated, and composed of smaller and larger spherolites, the enamel is cracked at the edges, the dentin shows a homogeneous structure *(Figs. 2, 3, 4)*. The enamel and dentin can hardly be distinguished by means of such examination.

With the replica-impression method [LOVAS, 1960] the surfaces were corroded with *N* HCl for an identical length of time, after which a replica was made with collodion. The differences between the three structural units appears very markedly when examined by means of a D-3 condensor. (Figs. 5-6-7). The sphaerolites of the cement layer show up much more plastically, the surface of the enamel is built up of hexagonal facettes, and longitudinal rib-like reliefs can be seen on the surface of the dentine layer.

Comparison with IR-spectrum

The IR-spectrum of the cement, enamel and dentine containing the original organic and inorganic fraction was taken with a UR-10 (Zeiss) apparatus in the 400—4000 cm^{-1} wave-number interval. The material was placed in a KBr -disc

(Fig. 8.). The spectra were compared with the IR-spectra taken by MOENKE [1962] under almost identical conditions. The spectra especially resemble the IR-spectra of the apatite, phosphorite samples of above author. According to these, in general the 400—1100 cm^{-1} band system denotes the bands of apatite, in the 1100—1700 cm^{-1} interval we can find the oscillations (1640 cm^{-1}) belonging to the carbonate and organic substances, in the 1700—4000 cm^{-1} interval can be seen the bands of OH and H_2O, possibly that of the NH_4^+ salts bound to the organic and inorganic structures

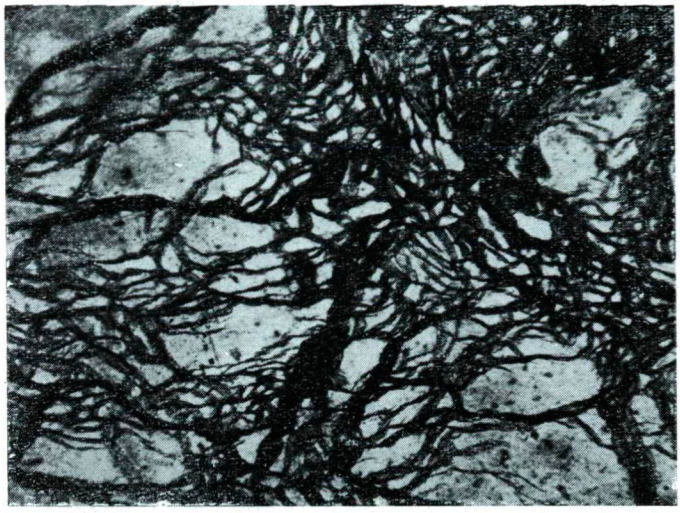

Fig. 3. A microscopic picture of enamel, in transmitted light, parallel nicols. Magn. 28:1.

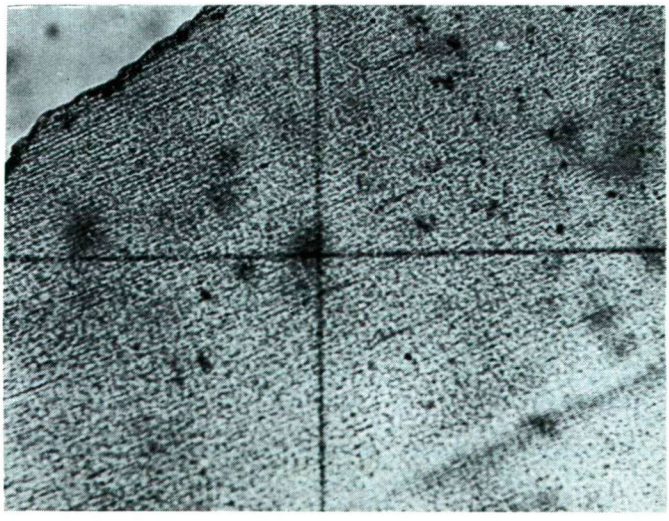

Fig. 4. A microscopic picture of dentine, in transmitted light, parallel nicols. Magn. 28:1.

with variable intensity. (It can be assumed that at 1600—1670 cm^{-1} AMID I; at 1500—1550 cm^{-1} AMID II; at 1230 cm^{-1} AMID III; at 660 cm^{-1} AMID IV; at 1410, 2420 and 2850 cm^{-1} CH_2—CO—NH bindings are seen to appear.)

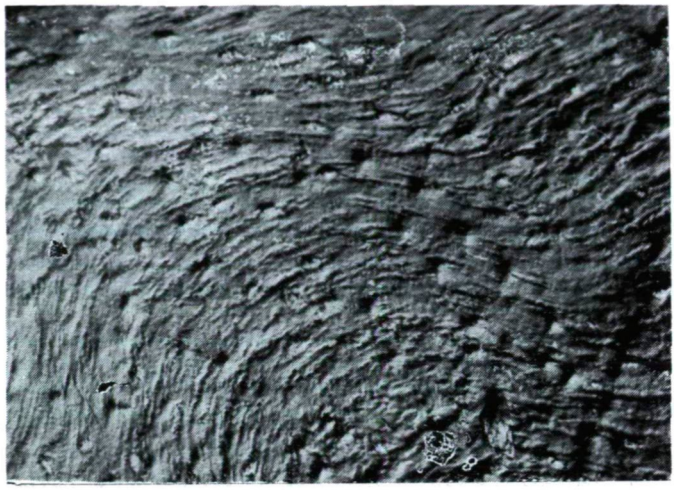

Fig. 5. The replica-impression picture of cement with a D-3 condensor. Magn. 310:1.

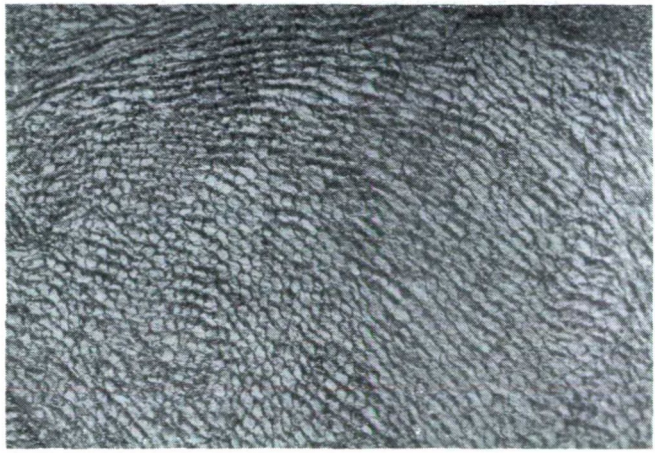

Fig. 6. The replica-impression picture of enamel with a D-3 condensor. Magn. 310:1.

When comparing the three spectra with one another, the similarity of the cement and dentin is found to be striking (more OH, organic material, carbonate), as well as their difference from the enamel.

The IR-spectrum of the organic fraction liberated from the inorganic material with EDTA was taken with a Unicam-SP 200 G apparatus in the 650—4000 cm^{-1} wave-number interval with the material in a KBr-disc *(Fig. 9)*. Though we did not touch upon the detailed evaluation of the spectra, the difference of the organic frac-

tion of the enamel layer from that of the cement and dentin layers is marked (730, 1550, 1735, 2360, 2950 cm^{-1} bands). The similarities and differences are also perceptible when the bands are compared quantitatively.

Comparison by means of thermoanalysis

The investigations were carried out with a Derivatograph apparatus of domestic made, with which the DTA-, DTG-, TG-relations were jointly analysed.

First the natural material was investigated. The cement, enamel and dentin layers were compared in the No. 2 platinum crucible under identical experimental conditions. On the basis of previous experiments the following programme was elaborated: Measurements: between 1,3—1,4 g. The volume of the inert material Al_2O_3 corresponded to the volume of the investigated sample.

The sensitivity of DTA, DTG was 1/10, the TG sensitivity was 500 mg. The motor and disc rate was 200, initial voltage 95 V, the situation of the nails: 3 rows of nails in a large disc. The samples were examined in furnace No. 1 under a quartz cup, without suction, in air atmosphere, in an interval of 20°C—1000°C. The derivatograms were evaluated on photo paper, then remodelled onto a scale of equal temperature, taking into consideration the intensity of the DTA—,DTG -curve *(Figs. 10 – 11 – 12)*.

Comparing the relations of the dentin DTA, DTG, TG *(Fig. 10)* with the data obtained during the investigations carried out on human dentin by BERÉNYI *et al.* [1970], a striking difference can be observed. The thermoanalytical processes taking place during heating can be interpreted as follows: The adsorptive and weakly bound

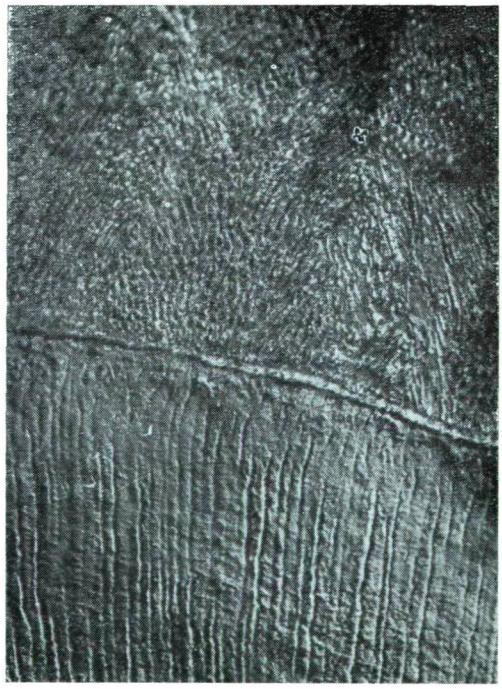

Fig. 7. The replica-impression picture of enamel (upper part) and dentine with a D-3 condensor.

water is eliminated with maximum rate from 178° C to 250° C. The beginning of the decomposition of the organic material of the tooth is closely correlated with this process. This decomposition can be compared to „cracking". The liberation of the water bound to the organic macromolecules, the initial decomposition and transformation of the organic structure, the desamination and decarboxylization of the amino acids takes place here. The process is composed of exothermic and endothermic reactions (404° exothermic and 471° C DTA-curve endothermic bend). The changes observable from 620° C on are also complex, the burning of the remaining

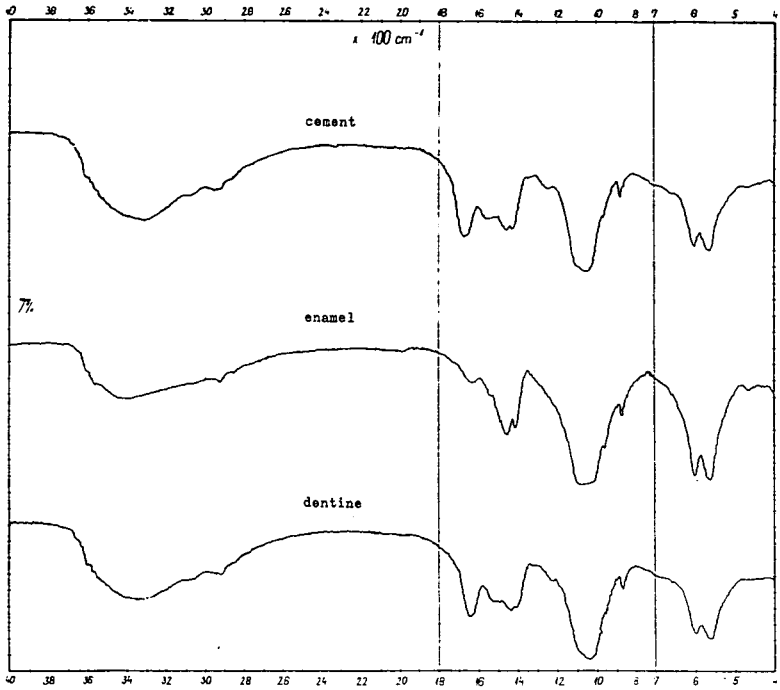

Fig. 8. The IR-spectrum of the structural components of an African elephant's tooth (charasteristic bands).

Cement cm^{-1}	Enamel cm^{-1}	Dentine cm^{-1}
	467	470
470	565	560
565	603	600
605	663	662
875	870	870
965	880	955
1050	960	1040
1240	1060	1230
1340	1415	1330
1420	1460	1410
1455	1540	1440
1668	1640	1640
2930	2850	2930
3080	2920	3070
3330	3400	3300

organic material (900° C DTA-curve maximum) predominates and covers the release of the CO_2 originating from the carbonate-apatite. In this respect we have distinguished three forms capable of liberating material.

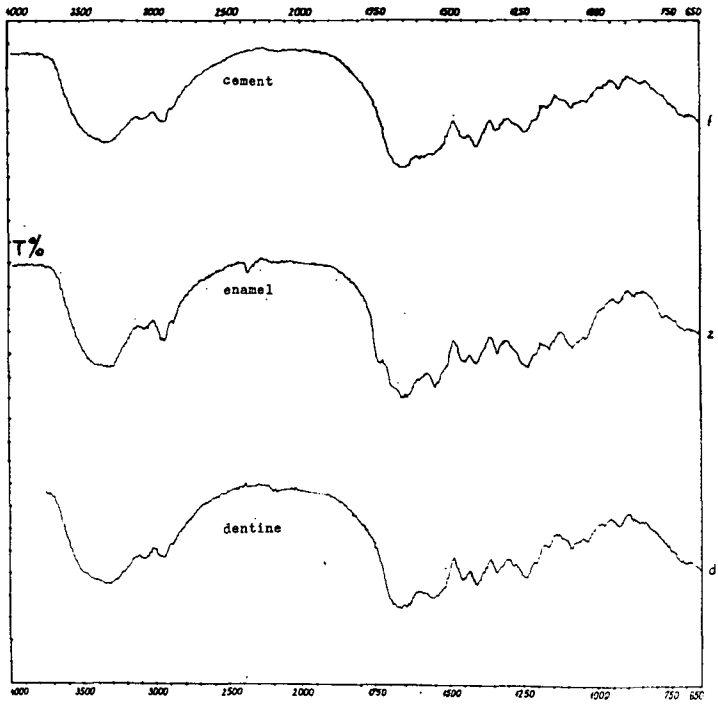

Fig. 9. The IR-spectrum of the organic fraction of pan African elephant's tooth isolated from it structural components

Cement	Enamel	Dentine
cm^{-1}	cm^{-1}	cm^{-1}
700	705	700
850	730	850
920	870	925
975	930	975
1030	1040	1030
1085	1080	1085
1168	1160	1165
1240	(1205)	1205
1335	1235	1240
1405	1335	1280
1442	1410	1335
(1550)	1450	1405
1650	1550	1450
(2160)	1650	1550
2875	1735	1660
2930	2360	2160
3080	2875	2875
3340	2930	2930
	2950	3080
	3075	3340
	3300	

The derivatogram of cement *(Fig. 11)* supplies us with an account of thermoanalytical properties similar to those of dentin. A more essential difference can be observed only among some of the TG-curve substance-liberating values, or in the decomposition taking place in the 600° C—1000° C temperature interval. The burning of the remaining organic material (DTA-curve, 917° C exothermic maximum) is more intensive, and the endothermic curves referring to the carbonate-oxy-apatite

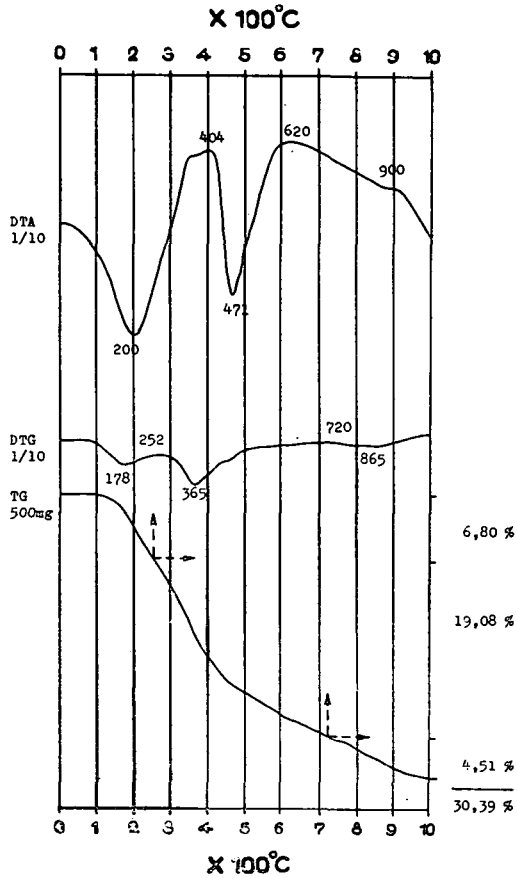

Fig. 10. The derivatogram of dentine in a platinum crucible.

also appear (DTA-curve 706° C, 842° C endothermal minimum). The thermogram differs sharply from the thermoanalytic data of human dental calculi of SIMON *et al.* [1969].

The enamel derivatogram *(Fig. 12)* differs totally from the derivatogram of cement and dentin. The essential difference can be observed in the relatively small amount of substance-liberation readable on the TG-curve. The difference can be explained by the fact that there is no endothermic process in the vicinity of 500° C.

In this case also the burning of the remaining organic material covers the endothermal processes marked by the decomposition of the carbonate-oxyapatite.

Comparing the thermoanalytical data of the Loxodonta enamel with the data of human enamel reported by BERÉNYI *et al.* [1969], the thermoanalytical processes may be said to be almost identical, the difference ensuing from the selection of the diverse DTA, DTG and TG sensitivities.

In the course of the experiments it was suggested that we must not count burning, but on slow "crack" processes in the platinum crucible in relatively oxygen-poor environment in the interval of low temperature. This decomposing process is catalytically influenced by the platinum crucible. To verify this, the heating of the samples was carried out in a ceramic crucible. LIPTAY et al. [1968] call attention to the catalytic effect of the platinum crucible and its elimination.

The thermoanalysis was performed in the ceramic crucible under experimental conditions identical to those of the platinum crucible. The converted and evaluated derivatograms are shown in *Figs. 13, 14* and *15*. A survey of the figures proves that our supposition was correct. In the case of the dentin and cement the DTA-curve

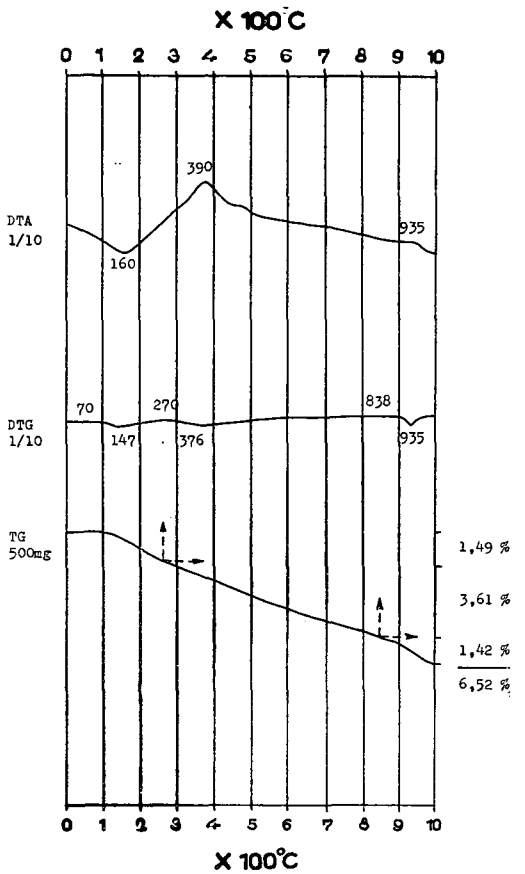

Fig. 11. The derivatogram of enamel in a platinum crucible.

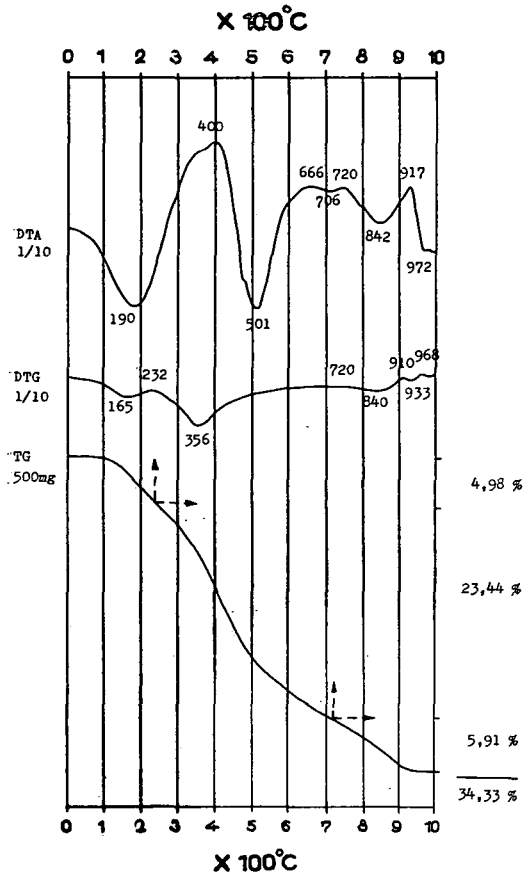

Fig. 12. The derivatogram of cement in a platinum crucible.

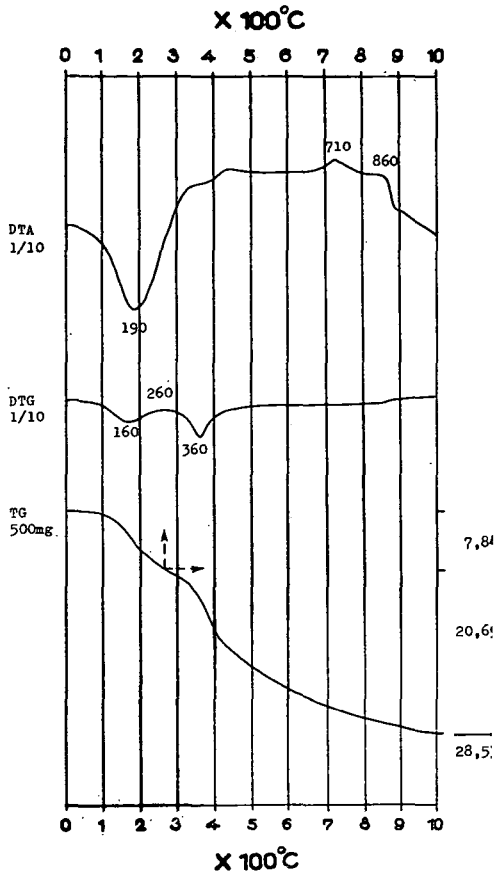

Fig. 13. The derivatogram of dentine in a cerar crucible.

changes denoting the exothermal and endothermal reactions appearing in the "crack--interval" had disappeared (or hardly appeared in the case of the cement) and the decomposition process of the organic material had shifted in the direction of the interval of higher temperature. (In dentin it takes place between 701° and 860° C, in cement at 865° C.) With this method the derivatogram of cement and dentine differs much more sharply from each other than in the platinum crucible. In the case of enamel, of course, these processes cannot be observed, since the separation of the endothermal and exothermal processes does not manifest itself in a platinum crucible, either. This fact can be explained by the small amount of the organic material. In a ceramic crucible, employing 200 mg TG sensitivity, the thermo-reactions separate much better in the interval of higher temperature.

We were not able to obtain satisfactory information about the nature of the inorganic material constructing some of the structural components when we carried out the investigations either in a platinum or in a ceramic crucible. Since we could not afford to use inert atmosphere (N_2 inert gases), we removed the organic fraction in NaOH + glycerine and examined the remaining inorganic material by employing a more sensitive programming. The investigations were carried out in a platinum crucible with 1/5 DTA, DTG sensitivity, 100 mg TG-sensitivity. The thus gbtained evaluated derivatograms are shown in *Figs. 16, 17, 18.* A survey of the fioures shows us that the exclusion of the confusing role of the organic material

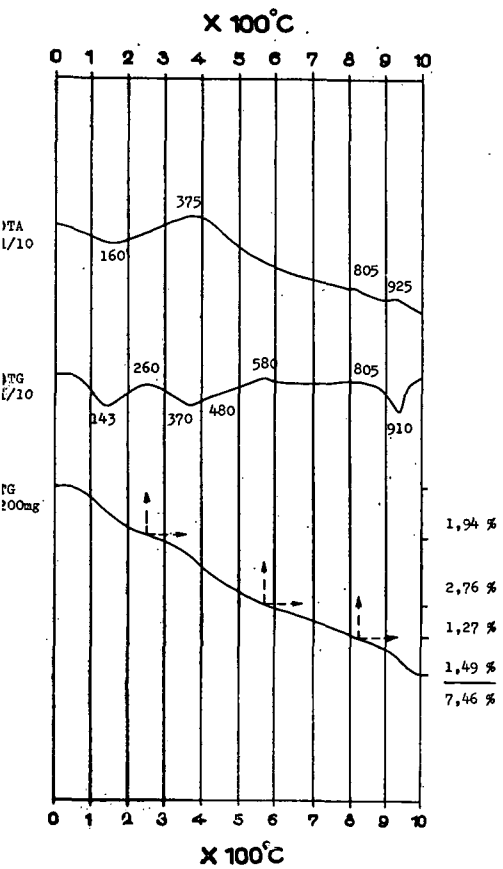

Fig. 14. The derivatogram of enamel in a ceramic crucible.

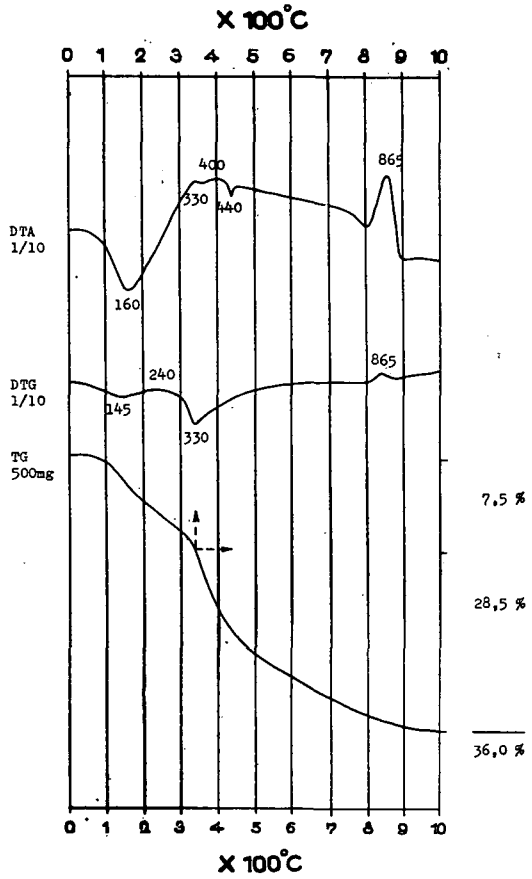

Fig. 15. The derivatogram of cement in a ceramic crucible.

was successful, though it can be assumed that some remainder of the organic material may still be enclosed by the organic structure. This organic material becomes partially hydrolysed and broken up into fragments. The thermoanalytical decomposition takes place as follows:

The adsorptive water evacuates by 240° C in the case of cement and dentin, in the case of enamel by 300° C. The OH^- bound to the inorganic structures detaches itself continuously simultaneously with the liberation of the OH^- bound to the remaining organic material as well as with the decarboxylization and desamination. This process can be followed in three steps in the case of the dentin, in the case of the cement in two steps, and in one step in the case of the enamel up to 700° C.

The decomposition of the carbonate-apatite structure begins at 700° C. The release of the CO_3^{--} takes place in two sharply separated steps. The CO_3^{--}, is bound taking into consideration the results of POSNER and DUYCKAERTS [1954] by Ca^{++} and Mg^{++}. It may be assumed that calcite and magnesite or even dolo-

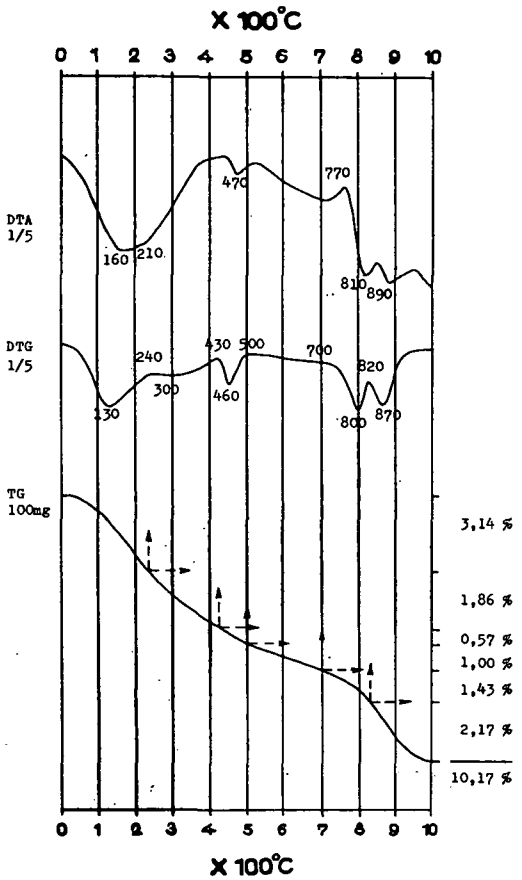

Fig. 16. The derivatogram of dentine, previously treated with NaOH-glycerine solution, in a platinum crucible.

mite are present in free state. It is to be noted that on the basis of the DTA investigations of SILVERMANN *et al*, there is no change in the thermoanalytical curve of dahllite, though, in the vicinity of 800° C, it releases some water enclosed in the apatite structure.

It is noteworthy that SCHRÄMLI and BECKER [1960] experienced and endothermal change in the course of their fluorapatite DTA investigations at 870° C.

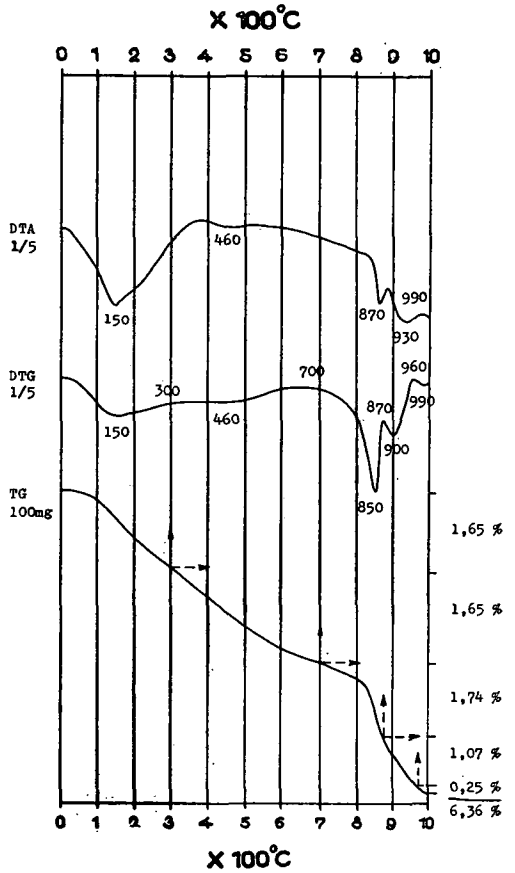

Fig. 17. The derivatogram of enamel, previously treated with NaOH-glycerine, in a platinum crucible.

As regard the enamel, a third small quantity of exothermal release of material can be observed from 960° C on, and in the case of the dentin and cement an exothermal process can be experienced simultaneously with the initial release of CO_2 (760° C, 770° C on the DTA curve). Exothermal release of material can be observed in the cement and not a transformation. The signals interpreting these exothermal processess can be explained by the final burning of the eclosed organic material.

The DTA, DTG, TG relations of the structural components analysed and pre-

pared under identical circumstances differ from each other, but here, too, can be observed the thermoanalytical similarity of the cement and dentin layers and their difference from the enamel.

DISCUSSION OF RESULTS. CONCLUSIONS

On the basis of the instrumental analytical investigations carried out on the three structural components of the Loxodonta tooth, we may summarize our findings as follows:

1. The difference between the three layers can be revealed by means of optical, IR-spectroscopical, and derivatographic methods. Assuming the existence of the diversified structure variations directed by the taxonic situation, such a comparison of modern and fossiliferous taxons is justified. The thermoanalytic method can be recommended for the comparison of the complete tooth as an organic-inorganic unity, but carried out in different crucibles, and performing the inorganic control for the purpose of interpreting the thermoanalytical processes. [We deem it advi-

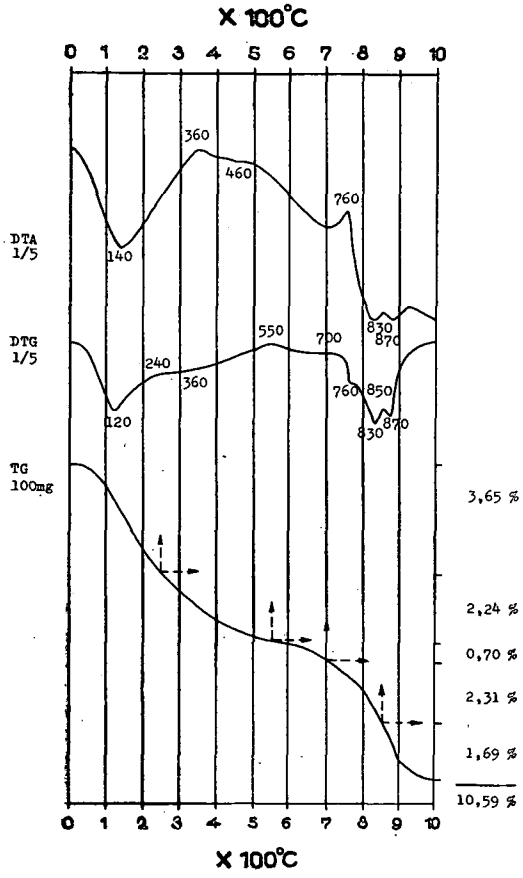

Fig. 18. The derivatogram of cement, previously treated with NaOH-glycerine, in a platinum crucible.

sable to perform the latter (inorganic control) investigation in inert atmosphere and to compare it with the NaOH-glycerine method used by us]. The IR-spectroscopic analysis, following the above-described preparation method is suitable for tracing the organic fraction. For deciding problematic cases and investigating fine structures the optical method is the most suitable, first and foremost the replica-impression using D-3 condensor investigation. This comparative method will play an important role in the analysis of the teeth of small-size mammals and in the identification of fragment material.

2. Despite structural differences and slight physico-chemical deviations, the similarity of the cement and dentin layers is striking. This similarity is represented by both the IR-spectroscopic and the thermoanalytic series of investigations.

These facts prove that the cement layer is not an externally deposited dental calculi-like formation, but a calcified structure constructed by collagen, which must by all means be reckoned with in comparative taxonomic respect.

3. Though the employed methods differ, the human dentin and enamel derivatographic data of the Loxodonta, verifying the taxon-specific differences demonstratable between the various taxons.

4. For the first time in the course of analysing the teeth derivatographically we succeeded in outlining the thermoanalytic data of the inorganic phase satisfactorily. Naturally, the final solution will be the investigation of the samples in inert atmosphere.

5. In this form the thermoanalysis (derivatography) is suitable for tracing fossilization by means of absolute index numbers in connection with investigations on fossiliferous evolutional lines. In the course of similar research on organic and inorganic components it will be advisable to supplement the investigations with the analysis of the trace elements of the fossils and embedding sediment.

SUMMARY

The author has analysed the cement, enamel, and dentin layers of the molar tooth of modern Loxodonta africana by means of optical, IR-spectroscopic, thermoanalytical (derivatographic) methods. The investigations clarified the organic and inorganic chemical difference of certain structural components. On the basis of the results it may be assumed that comparative systematic, paleontologic (identification of fragment material) work can be carried out with the mentioned methods. Supplementing the derivatographic method with trace-element investigations, the procedure will also be suitable for expressing fossilization with absolute index numbers.

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