J Therm Anal Calorim (2010) 101:63–70
DOI 10.1007/s10973-010-0903-9

Thermal properties of fossilized mammal bone remnants of the Urals

S. Votyakov · D. Kiseleva · Yu. Shchapova ·
N. Smirnov · N. Sadykova

RCCT2009 Special Chapter

Abstract Late-Quaternary material of various rodent species remnants (lower jaws and teeth) of different depth and age burials from zoogenic deposits in karstic cavities of the Urals (Russia) has been analyzed by thermogravimetry, differential thermal analysis, differential scanning calorimetry, and inductively coupled plasma mass spectrometry. Exothermic peaks position and shape as well as quantitative values of mass loss and heat effects (especially parameters of organic matter combustion at 200–600 °C) were found to vary significantly depending on bone's age and fossilization conditions. On the basis of correlation between bone organic component and corresponding concentrations of some trace elements, three different types of fossilization had been proposed. The obtained values of the organic contents in the bone remnants of similar type and location were used to identify different age admixtures as well as chronologically systematize large sample collections.

Keywords Bone · Teeth · Quaternary small mammals · Heat treatment · Thermal analysis

S. Votyakov · D. Kiseleva (✉) · Yu. Shchapova
Institute of Geology and Geochemistry UB RAS, Pochtovy per., 7, Yekaterinburg, Russia 620075
e-mail: kiseleva@igg.uran.ru

S. Votyakov
e-mail: Votyakov@igg.uran.ru

N. Smirnov · N. Sadykova
Institute of Plant and Animal Ecology UB RAS, 8 Marta str., 202, Yekaterinburg, Russia 620144
e-mail: NSmirnov@ipae.uran.ru

Introduction

Mammals' teeth and bones are unique living organic-polymer matrices. Their inorganic mineral phase consists of non-stoichiometric carbonated hydroxyapatite (dahllite) $Ca_{10-x}H_x(PO_4,CO_3)(OH)_{2-x}$ (about 70% by weight in bone, 78% in tooth dentin, and 99% in enamel) and can include 3–5% of carbonate. The organic constituent is predominantly presented by collagen (90%) and non-collagen proteins and lipids (10%) [1]. Dental and bony biominerals have a complex variable structure and morphology; they exist as crystal aggregates distributed among macromolecular organic network [2].

After mammals' death and burial, their bony and dental tissues undergo a number of diagenetic alterations leading to their lithification (fossilization). Due to the initial high porosity of the bone, its inorganic components are found in a state of chemical exchange with sediment that results in alterations of its chemical composition, grain size and shape, pore volume and shape, and secondary mineral deposition during fossilization [3].

Palaeonthological, archaeological, geological, and other studies in the relevant fields of knowledge seem impossible without a reliable chronological basis. The requirements to accuracy of dating any age or event depend on the time scale under study and the problems posed. For example, the dendro-chronological method can define the age with the accuracy up to 1 year, while the determination accuracy of isotope geochronology makes only some percent of a defined age. The above cases illustrate the absolute dating with classical methods based on radioactive decay of uranium (the so-called U-series), radiocarbon or other cosmogenic nuclides decay, and noble gases analysis. Recently, some new dating methods have been developed and widely applied, namely spectroscopy (electron spin resonance, luminescence, etc.), amino-acid racemization, determination of organic matter losses, chemical dating (uranium and fluorine tests, cation ratios), etc. [4].

Sometimes the absolute dating is of no importance, and one is to decide whether objects are synchronous or not, which is older or younger. This is a task for relative dating. There is a number of relative age estimation methods for fossilized bone remnants based on determination of the content and characteristic features of the preserved organic constituent, with thermal analysis playing a key role among them [5]. The use of up-to-date techniques to analyze thermal behavior of bony tissue contributes to solving the problem of organic matrix destruction (such as thermo-kinetic methods, thermal desorption coupled to mass-spectrometry determination of evaporated products) and applying the obtained data for burial environment and age reconstructions.

The aim of article is to study alterations of organic constituent of contemporary and fossil bone and teeth

Table 1 Description of studied deposits and remnants

Deposit	Date	Layer accumulation time	Probability of mixed-age remnants
Yamal Peninsula	Contemporary (collected in 2004)	Months	Insignificantly low
Vrangel Island	Contemporary (collected in 1983)	Months	Insignificantly low
Filin grotto, the Urals	Contemporary (XX century)	Decades	Low
Kybla 1, the Urals	Contemporary (boundary XX–XXI century)	Several years	Low
Dyrovaty Kamen, Chusovaya river, the Urals	ca. 13 kyr	ca. 1 kyr	Low
Idrisovskaya cave, the Urals	21–36 kyr	More then 10 kyr	High
Zhilishche Sokola cave, the Urals	ca. 40 kyr	Several kyr	Significant
Atambazchink, Kazakhstan	Oligocene, ca. 30 myr	?	?
Smotrovoy rock-shelter, the Urals			
Layer 1	Contemporary (XX century)	Several decades	Significant
Layer 2, horizon 4–7	Holocene	First kyrs	Significant
Sukhorechensky grotto, the Urals			
Horizon 1–2	250 years ago	First hundreds	Low
Horizon 3–5	900 years ago	ca. 300 years	Significant
Horizon 8–7	2 kyr	?	Low
Horizon 9–12	3 kyr	First hundreds	Low
Kybla 2, the Urals			
Layer 1	Contemporary (XX century)	Decades	Low
Layer 2	Contemporary (XX century)	Decades	Low
Layer 3	Late Holocene	Hundreds (?)	Low
Svetly rock-shelter, the Urals			
Layer 1	Late Holocene		Low
Layer 2	?		High
Layer 3	?		High
Layer 4	?		High
Layer 5	Late Pleistocene		Low
Starik rock-shelter, the Urals			
Layer 1	Late Holocene	Hundreds or first kyrs	Low
Layer 2	Middle Holocene (?)	Several kyrs	High
Layer 3	Early Holocene (?)	Several kyrs	High
Ushminskaya cave, the Urals			
Layer 1	Late Holocene	First kyrs	High
Layer 2	Late–middle Holocene	First kyrs	High
Layer 3	Middle Holocene	First kyrs	High
Mahnevskaya Ice cave, the Urals	Mikulin middle-Glacial—Valdai beginning	Kyrs	High
Skorodum, Omsk region	Eopleistocene		

remnants of small mammals by means of thermal analysis in comparison with changes of microelement composition of their inorganic phase considering different conditions and duration of fossilization, and to use these data to estimate the fossils' relative age and space heterogeneity of late-Quaternary locations.

Experiment

Materials and methods

The investigated material from 10 different late-Quaternary deposits of the Urals (Russia) consisted of bone and tooth remnants (lower jaws and teeth) of various rodent species (e.g., water vole—*Arvicola terrestris*, ungulate lemming—*Dicrostonyx torquatus*, etc.). The remnants were collected from different depth and age burials (from modern to ancient of 10,000 years or older) from zoogenic deposits in karstic cavities [6]. Some contemporary material was obtained from Yamal Peninsula and Vrangel Island (Russia). For comparison, the remnants of extinct rodent species from some sub-Quaternary deposits were analyzed—Eopleistocene dated *Allophajomys pliocaenicus* from Skorodum, Omsk region (Russia) and Oligocene dated *Cylindrodontidae* from Atambazchink (Kazakhstan). The total of 190 samples of bone and tooth were studied (Table 1).

SEM images of bone fragments indicate the organic component degradation and inorganic constituent conversion depending on fossilization conditions: destruction, porosity decrease due to infilling with secondary mineral deposits, peeling and cracking of bone tissue, bacterial attack, initial structure decomposition, and secondary mineral formation (Fig. 1).

Cleaned from surface pollution diastemal mandible fragments, cheek teeth and incisors were analyzed by Diamond TG-DTA (PerkinElmer) in the temperature range of 25 to 900 °C at heating rate 20 °C/min in air medium. A number of measurements were carried out by synchronous DSC and EI-QMS of evolved gases analysis on STA 449C Jupiter with QMS 403C (Netzsch) in the temperature range of 30 to 1000 °C at heating rate 20 °C/min in air medium. Mass measurement sensitivity was 0.2 μg, mass loss error $<0.1\%$, and thermal effects measurement sensitivity 0.06 μW.

The microelement composition of the samples (Li, Be, B, Na, Al, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, Cs, Ba, rare earth elements, Hf, Ta, W, Tl, Pb, Bi, Th, U) was studied by inductively coupled plasma mass spectrometry (ELAN 9000, PerkinElmer) after microwave digestion in a mixture of 0.4 mL H_2O_2 + 2 mL HNO_3 + 2 mL HF.

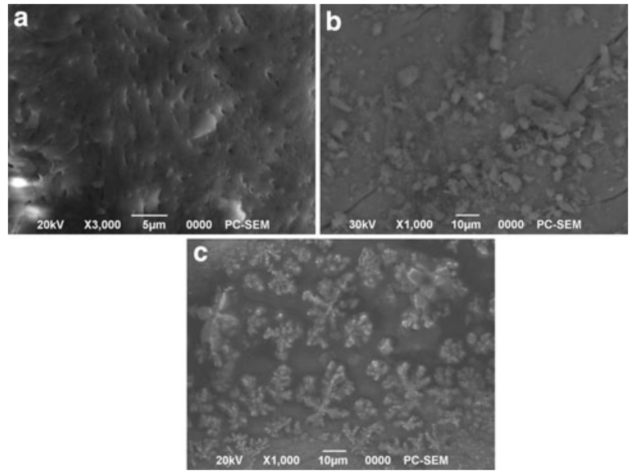

Fig. 1 Scanning electron microphotographs (JSM-6390LV, Jeol) of some investigated bone remnants. **a** Mandible of ungulate lemming (surface deposits of Yamal peninsula) was initially digested with gastric juice in an owl's stomach and then belched out packed in dense fur case which had prevented the bone from atmospheric (environmental) exposure. A good integrity of the bone is observed with Haversian systems and osteon structure being clearly visible. **b** Mandible of common vole (surface deposits from decomposed owl's pellets, Filin grotto, the Urals). Such adverse conditions and lack of substances favoring fossilization results in fast organics loss and collagen decomposition as well as cracking of bone surface and secondary mineral deposition. **c** Heel bone of bank vole (cave loam sediments, Idrisovskaya cave, the Urals) indicated significant degree of diagenetic alterations; its dark color and secondary mineralization in the form of dendrites probably caused by pyrolusite (MnO_2) formation

Results and discussion

Figure 2 illustrates typical thermal curves of the investigated bone and tooth fragments. The data on typical mass losses of bone and tooth remnants from some studied deposits are given in Table 2.

Mass losses in four temperature ranges registered on thermogravimetric (TG) curve are interpreted as follows [7, 8]: range A (25–230 °C)—adsorbed water loss; B_1 (230–400 °C)—structural water loss and low-molecular organic compounds combustion (denominated as "low-temperature organic content," e.g., non-collagen peptide like albumin); B_2 (400–600 °C)—high-molecular organic compounds combustion (denominated as "high-temperature organic content," mostly collagen); C (700–900 °C)—non-stoichiometric hydroxyapatite structural volatile compounds removal (e.g., CO_2) and their transition to stoichiometric compounds.

In order to analyze the character of bone and tooth tissue mass loss, we have carried out evolved gases determination. The results of mass-spectrometric analysis of gases evolved during dental tissue combustion are illustrated in Fig. 3b. Following [9], mass to charge ratio (*m*/*z*) values are interpreted as H_2O (18 a.m.u.), CO_2 (44 a.m.u.), NO

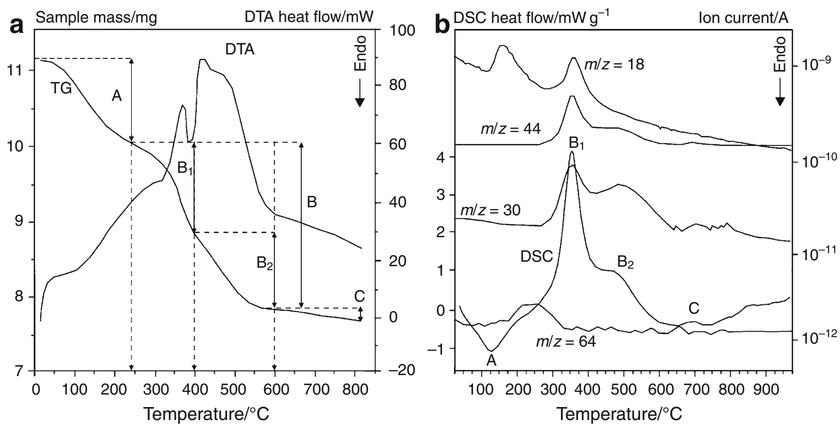

Fig. 2 Typical TG, DTA and DSC curves of lower mandible of bank vole (*Arvicola terrestris*) (**a**) and cheek tooth of ungulate lemming (*Dicrostonyx torquatus*) coupled with evolved gases mass-spectra (**b**)

(30 a.m.u.), and SO_2 (64 a.m.u.). According to the above concentrations (ion current intensities), gases make up the following sequence: $H_2O > CO_2 > NO > SO_2$. Water, carbon, and nitrogen oxides emission occurs synchronously with organic matrix combustion (230–600 °C). CO_2 and NO time-resolved mass-spectra are similar to differential scanning calorimetry (DSC) curves of the two-staged organic combustion process. A weak peak at about 700 °C is found on CO_2 mass-spectrum probably due to CO_2 removal from hydroxyapatite inorganic phase: $Ca_{10}(PO_4,\text{-}CO_3)_6(OH)_2 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + CO_2\uparrow$. SO_2 thermal behavior is worth mentioning for its mass-spectral peak at 280 °C, which does not obviously correspond to the organic bone constituent combustion. Obtained data are in agreement with represented in literature conceptions of mechanism of bones and teeth thermal decomposition [7, 8].

Exothermic peaks position and shape as well as quantitative values of mass loss and heat effects (especially parameters of organic matter combustion at 200–600 °C) were found to vary significantly depending on bone's age and fossilization conditions (Table 2; Fig. 3).

Two-stage process of organic constituent combustion studied in detail: stage B_1 was found to be characterized by the most intensive combustion with high rate of mass loss; stage B_2 implied a less intensive process with lower rate of mass loss. Figure 3 illustrates variations of organic combustion exothermic peaks position and their correlation for *Arvicola terrestris* mandible fragments from different horizons of Starik rock-shelter: first peak at 350–370 °C is lower in amplitude for younger bones from horizons 1, 3, 5, 11, and on the contrary, for the older bone fragments from horizons 18 and especially 21 it is slightly higher as compared to the second peak at 390–455 °C (the position of the latter is quite changeable). Thus, the features of exothermic processes of organic matter decomposition were considered sensitive enough for age and diagenesis conditions (fossilization environment) estimation.

Taking into account the above conclusion about bone's organic component loss dependency on its age and fossilization conditions, we tried to classify teeth and bone remnants according to peculiarities of their thermal behavior, in particular to high- and low-temperature organic contents. Variations of the total as well as high- and low-temperature organic contents of bone remnants in the studied deposits of different ages are given in Fig. 4. Deposits on X-scale are arranged according to their radiocarbon ages, and a trend indicating the decrease of organic matter content in bone remnants upon bone age increase is well observed. Nevertheless, it would not be correct to construct quantitative ratio of bone mass loss versus fossilization period span—due to the fossilization process conditions being different within the process distinct stages. Only relative aging of samples is acceptable, but still quite important for paleontologists.

Microelement composition of bone and teeth tissues has been studied. Two groups of elements have been assigned: trace elements with content 0.1–100 μg/g and ultra-trace elements with content less than 0.1 μg/g. The significant difference between different-aged samples has been observed in the content of rare earth (REE) and some other high field-strength (HFS) elements such as Sc, Y, Zr, Hf, Ta, Th, and U. Their concentration in bones increased by four orders of magnitude from contemporary and late Holocene to the oldest fragments: contrasting in concentrations and forms REE distributions normalized to Post-Archean Australian Shale (PAAS) [10] in bone fragments from different aged deposits are represented in Fig. 5.

Studying fossilization in different deposits, we observed the correlation between organic high- and low-temperature components content and concentration of REE and HFS elements in bone remnants (Table 3; Fig. 6). This correlation confirms the regular character; it depends on age and fossilization conditions, and points out to the bone's relative age. The developed approach made it possible to distinguish three major types (I–III) of fossilization (Table 3).

Table 2 Typical mass losses of teeth and bone remnants from some studied deposits

Deposit	Species	Sample mass/mg	Mass losses in different temperature ranges/mg				Exothermic peak position/°C		Total organic content/%
			25–230 °C (A)	230–400 °C (B_1)	400–600 °C (B_2)	600–800 °C (C)	B_1	B_2	
Cheek teeth									
Vrangel Island, fresh surface deposits	DT	9.6	0.81	0.82	0.53	0.17	365	400	15.5
Vrangel Island, fresh surface deposits	DT	10.2	0.86	0.91	0.56	0.17	364	402	15.8
Vrangel Island, fresh surface deposits	DT	11.5	0.92	1.03	0.63	0.19	364	397	15.8
Vrangel Island, fresh surface deposits	DT	9.0	0.76	0.77	0.49	0.18	362	395	15.3
Vrangel Island, fresh surface deposits	DT	7.1	0.56	0.64	0.39	0.13	361	388	15.9
Vrangel Island, fresh surface deposits	LS	17.3	1.14	1.33	0.90	0.30	366	412	13.8
Vrangel Island, fresh surface deposits	LS	21.5	1.75	1.76	1.17	0.37	365	412	14.8
Vrangel Island, fresh surface deposits	LS	24.9	2.04	2.00	1.40	0.41	362	427	14.9
Vrangel Island, fresh surface deposits	LS	19.9	1.77	1.78	1.12	0.34	363	414	16.0
Vrangel Island, fresh surface deposits	LS	23.5	1.97	1.80	1.32	0.33	366	419	14.5
Sukhorechensky grotto, horizon 3	MA	5.8	0.35	0.54	0.42	0.10	–	386	17.4
Sukhorechensky grotto, horizon 3	MA	5.7	0.34	0.62	0.35	0.12	–	381	18.1
Sukhorechensky grotto, horizon 3	MA	5.9	0.33	0.60	0.37	0.12	–	380	17.5
Sukhorechensky grotto, horizon 3	MA	7.4	0.44	0.72	0.41	0.14	–	382	16.3
Sukhorechensky grotto, horizon 3	MA	6.3	0.36	0.67	0.40	0.12	–	383	18.2
Sukhorechensky grotto, horizon 3	MG	6.6	0.31	0.67	0.24	0.15	–	368	14.6
Suchorechensky grotto, horizon 10	MG	10.1	0.41	0.93	0.39	0.18	310	380	13.7
Suchorechensky grotto, horizon 10	MA	6.6	0.33	0.71	0.30	0.23	302	385	16.8
Suchorechensky grotto, horizon 10	Mag	13.9	0.71	1.42	0.52	0.35	362	386	14.9
Zhilishche Sokola	DT	9.1	0.72	0.40	0.19	0.16	300	349	7.1
Zhilishche Sokola	DT	10.6	0.74	0.85	0.27	0.26	290	332	11.4
Zhilishche Sokola	DT	9.1	0.63	0.51	0.21	0.21	291	–	8.5
Diastemal fragments of lower mandibles									
Idrisovskaya cave	OC	12.5	0.90	1.05	0.67	0.24	355	390	14. 8
Idrisovskaya cave	OC	8.3	0.62	0.74	0.47	0.17	352	386	15.7
Idrisovskaya cave	CM	7.3	0.57	0.72	0.33	0.13	353	385	15.7
Idrisovskaya cave	DT	8.8	0.65	0.95	0.24	0.09	323	–	14.7
Idrisovskaya cave	LL	3.8	0.32	0.41	0.13	0.19	–	376	15.7
Idrisovskaya cave	MO	10.7	0.78	0.85	0.30	0.16	345	–	11.6
Idrisovskaya cave	MSP	8.2	0.68	0.83	0.33	0.15	–	378	15.3

Table 2 continued

Deposit	Species	Sample mass/mg	Mass losses in different temperature ranges/mg				Exothermic peak position/°C		Total organic content/%
			25–230 °C (A)	230–400 °C (B_1)	400–600 °C (B_2)	600–800 °C (C)	B_1	B_2	
Idrisovskaya cave	MSP	7.9	0.62	0.72	0.41	0.16	–	378	15.4
Zhilishche Sokola	DT	10.2	0.91	0.63	0.25	0.20	299	318	9.5

Note: *LL—Lagurus lagurus*, *DT—Dicrostonyx torquatus*, *MG—Microtus gregalis*, *MO—Microtus oeconomus*, *MA—Microtus* ex gr. *arvalis-agrestis*, *Mag—Microtus agrestis*, *LS—Lemmus sibiricus*, *MSP—Microtus* sp., *OC—Ochotona* sp., *CM—Cricetulus migratorius*

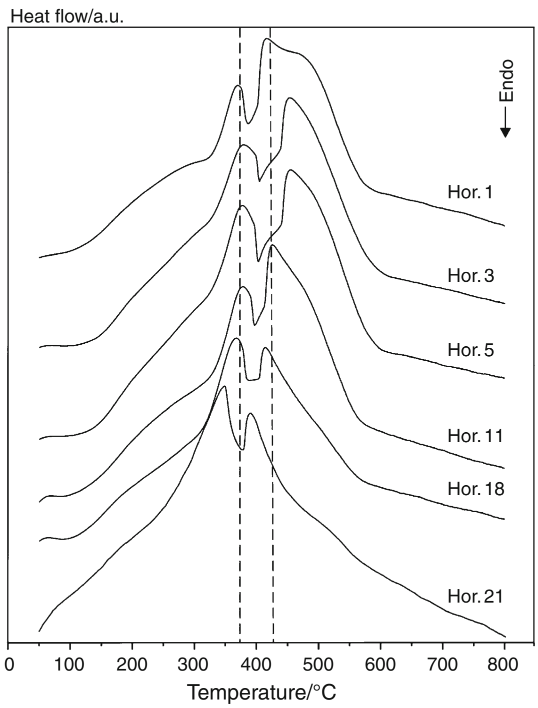

Fig. 3 Variations of DTA curves of *Arvicola terrestris* bone fragments in different horizons of Starik rock-shelter. *Dotted lines* mark average temperatures of the first (370 °C) and second (420 °C) exothermic peaks of organic matter combustion

All the examined contemporary and late-Holocene bone remnants corresponded to fossilization type I. Within this type, bones revealed lower (as compared to the enclosing rock) concentrations of REE and HFS elements (below 10 μg/g) and high content of organic compounds (19–25%). Early Holocene and Pleistocene remnants could be described as fossilization type II with organic content of 12–18% and REE and HFS elements concentration up to n · 10 μg/g. The bone remnants from Zhilishche Sokola deposit, dated about 40,000 years old, corresponded to fossilization type III. These remnants are characterized by high concentration of accumulated REE and HFS elements (up to n · 100 μg/g) and significantly lower organic content (about 9% in mandibles). An interesting sample from the alluvial Eopleistocene-aged Skorodum deposit studied for

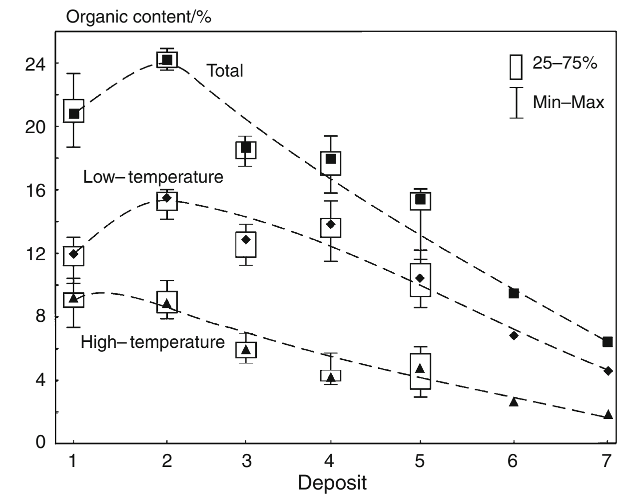

Fig. 4 Variations of the total, high- and low-temperature organic content of bones and teeth remnants in the studied deposits of different age and location: 1—Yamal Peninsula and Vrangel Island, surface deposits; 2—Kybla 2, layer 3, soil burial; 3—Starik rock-shelter, horizon 18, gray sandy loams; 4—Dyrovaty Kamen', river Chusovaya and Svetly rock-shelter, horizon 14–16, clay loams; 5—Idrisovskaya cave; 6—Zhilishche Sokola cave; 7—Skorodum

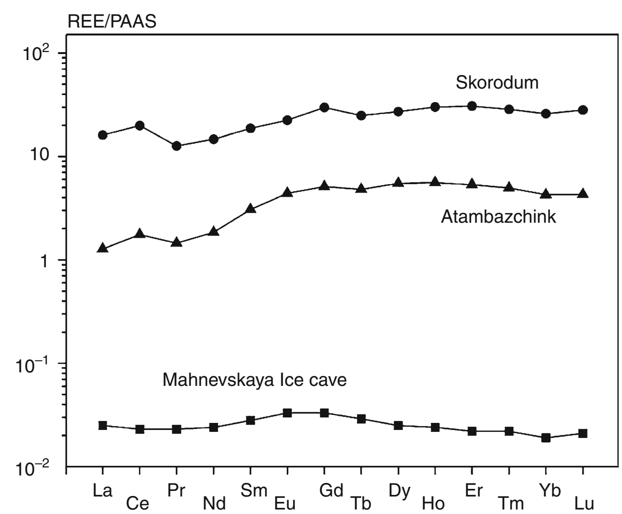

Fig. 5 Variations of REE distributions normalized to Post-Archean Australian Shale (PAAS) [10] in bone fragments from different-aged deposits

Table 3 Fossilization types based on thermal analysis and sample microelement composition

Fossilization type	Characteristics		Age	Deposit description, examples
	Total organic content/%	REE and HFS elements content/ μg g^{-1}		
I	19–25	≤10	Contemporary	Fresh surface deposits of karstic rock shelters; not-fossilized, unburied carnivores' food debris (Yamal Peninsula, Vrangel Island)
			Several hundred or thousand years	Initial stages of fossilization of the remnants embedded in gray sandy loam sediments (Filin grotto, Kybla 1)
			Not older than several thousand years	Embedding within soil active layer (Smotrovoy rock-shelter, Suchorechensky grotto)
II	12–18	n · 10	Early Holocene	Embedding in gray sandy loam layer (Starik rock-shelter, horizon 18)
			12000–13000 years	Cave loam sediments (Dyrovaty Kamen', r. Chusovaya)
			ca. 20–40 kyr	Cave loam sediments (Idrisovskaya cave)
III	9	n · 100	ca. 40 kyr	Cave loam sediments (Zhilishche Sokola)

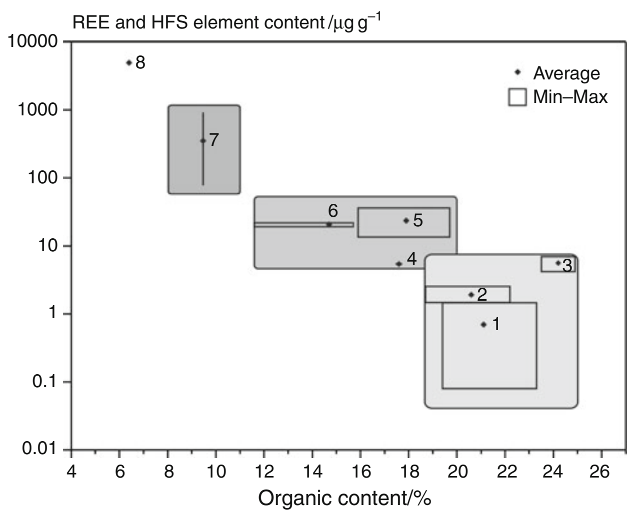

Fig. 6 Total organic content versus RE and HFS elements content in bones and teeth from various deposits: 1—Yamal Peninsula and Vrangel Island, surface deposits; 2—Kybla 2, layer 3, soil burial; 3—Starik rock-shelter, horizons 5–11; 4—Starik rock-shelter, horizon 18; 5—Dyrovaty Kamen', river Chusovaya; 6—Idrisovskaya cave; 7—Zhilishche Sokola cave; 8—Skorodum

better visualization of the trend obtained (No. 8 in Fig. 6) is characterized by very low organic content (slightly over 6%) and very high concentration of REE and HFS elements (4900 μg/g).

Conclusions

Thermal analysis proved to be a powerful tool for investigation of organic constituent's conversion degree of modern and ancient small mammals bone and teeth remnants. The parameters of exothermic peaks and mass losses of organic combustion stages B_1 and B_2 (200–600 °C) corresponding to thermal transformation of low- and high-molecular organic compounds appeared to be the most informative. On the basis of comparative analysis of thermal processes, three different types of fossilization have been proposed. Methods of thermal analysis were used to study contemporary and fossil mammal bones and teeth from different late-Quaternary deposits of the Urals (Russia). The obtained estimates of the organic constituent in the remnants series of similar type and location were used to identify mixed-age remnants as well as chronologically systematize large sample selections.

Acknowledgements This article was supported by the Russian Fund for Basic Research (Grant No. 08-04-00663-a, 09-p-4-1001, and 09-C-4-1015).

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