Thermoluminescent method of dating applied to fossilized animal remains

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Abstract. The feasibility of applying the thermoluminescent method to dating of fossilized paleontological animal remains is investigated. Relatively easy application and a wide range of chronological time periods over which the method produces reliable results with minimized uncertainties under an optimized experimental setup, make the method highly suitable for fossil dating. Mammoth remains from a collection of an archaeological museum were dated using samples of teeth, bones, and tusks. We determined two distinct age regimes of the investigated mammoth remains: (1) ranging from 12 to 28 thousand years (the bulk of the samples) and (2) from 40 to 45 thousand years. For isolated samples, the estimated ages were above 100 thousand years.

1. Introduction

Fossilized animal remains, which are usually found as fragments of calcareous or apatite skeletons associated with various amounts of organic matter, are traditionally dated with the radiocarbon method [1], [2], [3], [4], [5], [6]. However, due to the limited ability of the radiocarbon method in determining ancient ages, there is a need for new approaches to dating of paleontological remains, as dating of such materials, e.g., of mammoth remains, is highly relevant from the standpoint of paleoclimate studies [7] [8], [9].

Despite considerable interest in the study of the earth climate, especially in the recent decades, the nature of climate change processes continues to be an active area of research. In order to separate natural and anthropogenic climate change, it is necessary to have the knowledge of pre-anthropogenic climate fluctuations. Such knowledge can be derived from the analysis of natural objects that have high sensitivity to regional climate conditions. In particular, ancient remains of animals and human settlements buried in Quaternary deposits of continental and island land masses can be successfully used for paleoclimate studies.

According to modern understanding, mammoths have inhabited the earth since about 2 million years ago and disappeared about 10 thousand years ago [4], [5], [6], [7], [8], [9]. The mammoths coexisted with various species of the fauna, including up to 80 types of mammals. The extinction of the mammoth is a part of the mass extinction of land mammals that began about 40 thousand years ago. This degradation process eventually led to a complete disappearance of more than 30 species of animals. One of the hypotheses of the mammoth extinction attributes the process to drastic climate changes at
the turn of the Pleistocene-Holocene, which led to irreversible transformation of habitats, reduction and disappearance of sufficient food supply, and increased interspecific competition [1], [2], [3], [4], [5], [6]. During the Quaternary period, periodic climate changes and alternations of glacial and interglacial epochs took place. Climate scientists define four major glacial and interglacial periods, over which there were superimposed localized episodes of cooling and warming, occurring with certain periodicity. Dating of fossilized animal remains (i.e., determining the time of their burial in the sediments or ice) can potentially provide rich information about regional climate changes. Over the years, there have been numerous finds of frozen fragments and whole carcasses of adult and juvenile mammoths in several regions of Siberia, the Russian Far East, and Alaska.

As mentioned above, while mammoth remains are traditionally dated using radiocarbon method, the application is often limited by extremely ancient ages and insufficient amount of collagen present in the fossils.

One of the promising methods for determining the age of archaeological objects is the thermoluminescent (TL) method, which is based on the effect of storing non-equilibria charge carriers at local levels, their subsequent release from traps, and radiative recombination induced by a thermally activated process [10], [11], [12], [13]. When the magnitude of the measured effect is proportional to the ionizing radiation dose and if the rate of dose accumulation (dose rate) is known, it is possible to determine the irradiation time and therefore, the age of the object [11], [12].

Over several years, we have been developing an archeological dating method based on the TL analysis that employs equipment originally designed for individual dosimetric monitoring [14], [15], [16]. An important feature of the method is the use of TL detectors TLD-K, developed by our team, that are derived from glass ceramics and are characterized by near-perfect soil- and bone-equivalence [17]. These detectors allow accurate detection of natural background radiation doses absorbed by both archaeological ceramics and bone remains, as well as reliable dosimetry under laboratory irradiation.

To date, the TL method has not been widely used in paleontological dating, likely because of the presumed temperature instability of organic remains. Thus, the TL dating application proposed here has a certain degree of novelty and the applicability of the method to the specimens of organic origin must be thoroughly evaluated. To achieve reliable age assessment and minimize age uncertainties, one of the objectives of the present study was to design an optimal setup for the TL dating procedure of organic specimens (i.e., sample preparation procedures, measurement regimes for TL detection in the range of 200-350 °C, and laboratory irradiation doses).

In the present study, we analyze a number of samples from museum displays, representing a variety of locations in Western Siberia, and provide age estimates of mammoth remains based on the samples of teeth, bones, and tusks indicating at burial into Quaternary deposits. The relative ease of application and suitability to a wide range of chronometric periods (wider than for the radiocarbon method) suggest that the TL method is a potentially promising approach to dating of fossilized remains. Undoubtedly, there is a demand for improving dating capabilities, especially in the age ranges between tens and hundreds of thousands of years, where the radiocarbon method has limited applicability. For certain chronometric periods, the TL ages could be directly compared with the ages obtained for the same specimens by the radiocarbon method.

2. Study objects

We investigated fragmentary paleontological finds of animal remains, collected in Kemerovo Region of Russia, from the permanent collection of the archeological museum of Kemerovo State University (KemSU) (Table 1).

Figure 1 shows photographs of the paleontological fragments described in Table 1. From the middle part of each paleontological fragment, we extracted small, approximately homogeneous sections, weighing on the order of several grams. These sections were then separated into multiple chip samples of identical size, weighing about 10 mg each. The chip samples were used to determine the optimal heating ranges and the temperature range of TL signal registration, and to evaluate homogeneity of
sample composition.

Table 1. Description of the paleontological finds of mammoth remains.

| No.   | Object type                        | Site (year) of the find          | Museum location |
|-------|------------------------------------|----------------------------------|-----------------|
| 22.4  | Mammoth bone (ulnar, left)         | Tom River                        | Exposition      |
| 22.8  | Mammoth tusk                       | Shestakovo, Kiya River (1976)    | Exposition      |
| 22.9  | Mammoth tusk                       | Shestakovo, Kiya River (1976)    | Exposition      |
| 22.16 | Mammoth tusk                       | Tom River                        | Archives        |
| 22.24 | Mammoth tooth                      | Yurga, Tom River                 | Archives        |
| 22.51 | Mammoth bone (shoulder blade)      | Unknown                          | Archives        |
| 22.56 | Mammoth tooth (fragment)           | Zelenogorskiy, Tom River         | Exposition      |
| 22.58 | Mammoth (fragment)                 | Komissarovski                    | Archive         |

Chip samples with the highest reproducibility of the TL curve over three replicates were selected for further analysis and were also used to prepare powdered samples. The process of powder preparation turned out to be extremely labor-intensive because the samples were very hard. The final stage of sample preparation consisted of grinding up each sample in an agate mortar and extracting selected grain size of the powder. The results obtained from the analysis of the powdered samples turned out to be more reliable and reproducible due to more uniform heating and larger sample surface area.

The analysis of the photoluminescence of the selected samples showed that in the luminescence spectrum there is a luminescence band with a maximum in the 450-nm region (Figure 2). The luminescence spectrum is nearly identical to that of a modern human tooth, which indicates that the mineral component of the fossilized fragments is well-preserved [18].

The inorganic components of bones are known to consist of carbonate hydroxyapatite, a carbon-containing calcium phosphate. Hydroxyapatite, Ca_{10}(PO_{4})_{6}(OH)_{2}, is the primary crystal found in mineralized tissues; it makes up to 97% of tooth enamel and 60-70% of bone tissue [18]. When hydroxyapatite is irradiated with ionizing radiation, oxygen vacancies are formed mainly in the phosphate groups, creating centers in the forbidden zone with a depth of about 3.45 eV; these centers are likely responsible for the observed luminescence. The luminescence intensity of a healthy human
The tooth is markedly different from the decaying human tooth (Figure 2), which could potentially explain (in addition to the age differences at the time of burial) some of the large differences in the observed TL intensities (i.e., healthy vs. diseased animals).

Figure 2. Photoluminescence of a tooth of a human and a mammoth (study object 22-56). 1-3—luminescence under the 350-nm excitation of 1—mammoth tooth, 2—healthy human tooth, 3—decaying human tooth; 4—luminescence excitation spectrum

3. Methodology and experimental setup

The choice of the optimal sample size and heating regime depends on the TL characteristics of a particular material and thus, must be determined prior to the primary analysis of the sample series. Ideally, the highest TL registration sensitivity can be achieved on thin layers of a powdered sample with uniform grain size, in a cuvette that is ~1 cm in diameter.

In the present study we used a modified DTU-01M dosimetric complex, which is characterized by high sensitivity to weak luminous fluxes, has the registration capacity with the temperature range of TL detection extended up to 450 °C, and the capability to vary heating rate from 2 to 8 °C/sec. The same instrumentation, but with amended settings (standard for dosimetric applications), was used for the dosimetric measurements of the laboratory irradiation, as well as for determining the background radiation dose rate of the study objects using soil- and bone-equivalent TLD-K detectors [17]. To determine the background radiation dose rate, detectors TLD-K were placed into the soils at the sites of artifact extraction [14] for a period of at least 20 days. The dose of the laboratory exposure was also determined with the TLD-K detectors, which were placed directly into the sample that was irradiated.

Laboratory irradiation of the samples was carried out by the penetrating gamma radiation of radioactive isotope cobalt-60 using РХМ-γ-20 experimental complex. In order to ensure reliability, readings of at least three replicate detectors were averaged to determine the radiation dose of each irradiated sample. The TL measurements were performed five days after the laboratory irradiation. The chronometric age of the samples was calculated using the following formula:

$$A = \frac{D - S_0}{S_{\text{irrad}} - S_0 - P}$$ (1)

$A$ is the age, years;
$D$ is the laboratory radiation dose, cGy;
$P$ is the annual background dose rate at the site of the paleontological find, cGy/year;
$S_0$ is average relative intensity (light sum) of the TL peak of the sample, arb. units,
$S_{\text{irrad}}$ is average relative intensity (light sum) of the TL peak of the irradiated sample, arb. units.
The uncertainty in the determined age consists of the measurement error in the TL of irradiated and non-irradiated samples and the uncertainty in the laboratory radiation dose and background dose rate. The error in the laboratory radiation dose did not exceed 3%. The reproducibility of the TL characteristics of a particular object depends on the consistency of the mineralogical composition of the samples; the uncertainty for our samples did not exceed 3%.

As a side note, in addition to the above application, the TLD-K detectors developed and mass-produced in our group, can be used for a full-scale dosimetric monitoring. Such monitoring can provide a fairly simple and reliable method of evaluating the potential radiation hazard of previously identified sites negatively affecting the environment and human populations in the Arctic exploration regions, as well as to identify localized radiation hotspots. The results of such full-scale monitoring can also provide valuable information for the geological survey of the Arctic.

4. Results
We were able to register the TL signal in the temperature range of 200–350 °C for nearly all study objects. Heating to a higher temperature resulted in charring of some of the samples with the release of a characteristic smell.

Figure 3 shows TL curve examples of non-irradiated powder samples. The weights of the powdered samples and the measurement regimes were practically identical, but the intensity of the registered signals varied greatly among the samples. The TL signals of the investigated fossilized fragments were about two orders of magnitude larger than the intensities of archaeological ceramics in [14], [15].

Figure 4 shows TL curves of selected powder samples of the paleontological remains irradiated with the laboratory dose of 40 Gy. The temperatures of the TL maxima in irradiated and non-irradiated samples were nearly identical, located at above 300 °C (under given experimental conditions), thus enabling long preservation of the stored light intensity (at least $10^5$ years).

The maximum intensity for all irradiated samples was slightly shifted towards lower temperature ranges, which indirectly suggests temperature de-excitation of the low-temperature part of the peak in the original (non-irradiated) samples. Following irradiation, the samples produced an afterglow caused by shallow traps (that is why it was necessary to rest the samples after irradiation for several days), but there were no low-temperature maxima in the region of 120–150 °C, which are typical of archaeological ceramics due to the presence of quartz [14], [15].

![Figure 3. TL curves of non-irradiated selected powdered samples of the paleontological remains.](image1)

![Figure 4. TL curves of selected powdered samples of the paleontological remains irradiated with the dose of 40 Gy.](image2)

The average annual radiation background delivers a dose load of 0.45 cGy/year to the soils of Kemerovo Region (as determined at archeological excavation sites during TL dating of ceramic objects) [14], [15], [16]. Given the laboratory irradiation dose determined by the TLD-K detectors and assuming
the average annual background radiation of 0.45 cGy/year, the calculated ages of the bulk of the samples range from 12 to 28 thousand years. For several samples, the ages ranged from 40 to 45 thousand years. There were several isolated samples with unrealistic ages of above 100 thousand years.

Figure 5 shows an example of the dose dependence of the signal accumulation for ~10-mg chip samples extracted from the study object 22.8 (Table 1), which was the most homogeneous. The average age estimated from the exposure to three different doses was 20,200±400 years.

![Figure 5. Dose dependence of the TL signal accumulation for the samples of the study object 22.8.](image)

Difficulties in providing age estimates arise because of the large variability of the measured TL intensities among the original objects, as well within each object, associated with the large heterogeneity of the object composition.

It should be emphasized that the goal of this study was to demonstrate the potential feasibility of the application of the TL method of dating to the paleontological animal remains, while the precise age determination is beyond the scope of this work. To the skill of TL age determination, further studies are needed, where TL dating could either be applied simultaneously with other methods to the time periods over which other methods, e.g., radiocarbon dating, can produce reliable results; or applied to the objects that have already been reliably dated by other methods.

5. Conclusions
The study investigated the feasibility of applying the TL method of dating to fossilized paleontological remains of animals. The research was carried out on paleontological finds provided by the Kemerovo State University museum. We analyzed a number of fossilized objects collected from different locations in Kemerovo Region.

In order to obtain reliable experimental results, a long sample preparation procedure was required to ensure that the TL signal could be obtained from bone, tusk, and teeth samples for inferring their age. We observed large variability in the TL characteristics of non-irradiated remains, depending on the places of their extraction, which allows for the initial quality control of the material. There was also a significant variation in the TL intensity within a single sample due to the strong heterogeneity of the bone tissue composition [18]. The choice of methodology for the age assessment included selecting sample preparation procedure, measuring setup (heating regime, temperature, sample size), and radiation dose to obtain reliable results while minimizing the errors in age estimation.

We conclude that the TL method can be used to estimate the age of animal fossils, especially when using teeth and tusks as study objects. Mammoth remains were dated based on the samples of teeth, bones and tusks likely from the burials in Quaternary sediments. From the analysis of the
thermoluminescence curves we determined two distinct age regimes of the investigated mammoth remains from the museum collection: (1) 20±8 thousand years old (the bulk of the samples) and (2) 43±3 thousand years old. Isolated samples produced unrealistically old age of ≥ 100 thousand years. The obtained dating results could be substantially refined first by ensuring that the samples have not been previously exposed to high temperatures, high light levels, and other experimental treatments after their excavation and during the entire period of storage; and second, by a more precise determination of the background dose rate at the burial sites.

The age of 40±5 thousand years agrees with the results of the dating analysis of bone collagen, muscle tissue, and mammoth hair performed at the University of Georgia in the United States, as well as the results of the analysis of bone collagen at the University of Groningen (the Netherlands) [1], [2], [3], [4], [5], [6]. Some studies based on uranium-thorium method date animal remains at 130±9 thousand years [1], [2], [3]. In the Novosibirsk Center for the Collective Use of the SB RAS "Geochronology of the Cenozoic", which uses accelerator mass spectrometer, radiocarbon dating of mammoth bone produced the range of ages from 44.5 to 12.7 thousand years, which also agrees well with our estimates. It has been proposed that the youngest populations of woolly mammoth were likely present on the islands (Wrangel Island—dated at about 3.7 thousand and St. Paul Island, Alaska—dated at about 5.6 thousand years) [3], [4].

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