Investigation of Mammoth Tusk *Mammuthus Primigenius* by Thermogravimetry and X-ray Diffraction Analysis

T M Solovev¹,*, E S Petukhova¹, G V Botvin¹, T A Isakova¹, V V Pavlova¹

¹Federal Research Centre “The Yakut Scientific Centre of SB RAS”, 2 Petrovskogo str., Yakutsk 677000, Russia

*E-mail: tuskulsolovev@yandex.ru

**Abstract.** The article represents the results of the research of the mammoth tusk *Mammuthus Primigenius* using thermogravimetric (TGA) and X-ray diffraction analysis (XRD). The stages of thermal destruction of mammoth tusk components and their temperature limits are revealed. XRD of mammoth tusk showed that heat treatment leads to a change in the structure of the mineral component of the material under study from hydroxyapatite (HAP) to whitlockite. It was found that this process is caused by the presence of magnesium ions in the crystal lattice of HAP.

1. Introduction

Due to the presence of permafrost in the territories of the Arctic zone of Eurasia and North America, the tusks of mammoths *Mammuthus primigenius* and other remains of mammoth fauna are well preserved [1, 2]. Mammoth tusk is characterized as a unique natural raw material with increased physical and mechanical properties, so that since ancient times it has aroused a certain interest as a raw material for the manufacture of various tools and devices, as evidenced by numerous archaeological finds [3]. Now the mammoth tusk, is a complete analog of the African elephant tusk, is actively used in the bone-cutting art.

Currently, the research and production of mammoth tusks are conducted mainly on the coast of the Arctic ocean, in the lower reaches of major rivers (Lena, Yana, Indigirka, Alazeya, Kolyma) and on the Novosibirsk Islands [2, 4]. According to statistics, the demand and production volumes of this raw material are only increasing [4]. At the same time, issues of preserving and improving the quality of extracted raw materials are becoming urgent. It is worth noting that scientific research on the properties, composition, and structure of mammoth tusks is conducted relatively little. A more detailed and in-depth study of this object would allow us to gain new knowledge about this unique biogenic raw material, which in turn would contribute to the development of new technologies and tools for its processing. Research aimed at creating polymer and ceramic composite materials based on secondary biogenic mineral raw materials looks promising.

It is known that the mammoth tusk is a composite material that consists of an organic part – collagen (20-30 %), mineral part – HAP (60-70 %), and water (10 %) [5]. Scientific interest is aroused by HAP, which by its structural characteristics belongs to a large group of minerals – apatite, and it is the main component of bone and dental tissues of animals and people. Due to its unique properties, calcium apatite is widely used both in instrumentation and medicine. In particular, HAP successfully serves as a basic component of synthetic materials for orthopedics and dentistry.
A detailed study of the structure of HAP is justified by its ability to wide variations of ion substitutions, which in turn significantly change its physical and chemical properties [6]. HAP of mammoth tusk has anionic and cationic substitutions in its structure [7-9]. These are mainly magnesium, sodium, and carbonate anion cations. The role and influence of these substitutions on the physical and chemical properties of the mammoth tusk *Mammuthus Primigenius* have been poorly studied. Therefore, in this work in order to determine the composition and phase transformations occurring during the heat treatment of the mammoth tusk *Mammuthus Primigenius* TGA and XRD was performed.

2. Materials and methods

As samples for research, bone-cutting waste were used, which were small fragments of the tusk. Before conducting research, tissue samples were ground to a powdery state.

To assess the composition and detect the content of impurities using an energy-dispersive X-ray spectrometer (Jeol JSM-6480LV) an elemental analysis of the samples was performed.

XRD is widely used in the study of the structure of crystalline substances, allows to identify the mineral components of unknown materials with high accuracy, and to clarify and decipher the composition and features of the crystal structure of a known substance. In this work the XRD was performed on a diffractometer D2 PHASER (Bruker, Germany). The analysis was performed under the following conditions: CuKα-radiation 30 kV, 10 mA; interval 4.5-65˚ (2θ˚). The minerals were identified using a database PDF-2/Release 2011.

Thermal analysis, as well as XRD, is a method for studying the phase composition of a multi-component substance. In contrast to XRD the method is based on the flow of various physical and chemical processes in the substance when heated. In the work the TGA was performed on asynchronous thermal analysis device STA 449C Jupiter (NETZSCH, Germany). The samples were heated in a crucible of PtRh from room temperature to 1000 ºС with a heating rate 10 ºС/min in an inert environment (argon).

All experiments were performed in Diamond and Precious Metal Geology Institute SB RAS (Russia, Republic of Sakha (Yakutia), Yakutsk).

3. Results and discussion

Table 1 shows the results of the elemental analysis of the studied mammoth tusk sample by energy-dispersive X-ray analysis. It can be seen (Table 1) that in addition to the standard elements for HAP – oxygen, phosphorus, and calcium, the sample contains magnesium. Taking into account the propensity of HAP to ion substitution, it should be assumed that the HAP in the studied samples is represented in the magnesium-substituted form $Ca_{1-x}Mg_x(PO_4)_6(OH)_2$. It was found that the stoichiometric ratio of Ca/P for the studied sample is 1.61, which is slightly different from the theoretical values of this value for pure HAP, which is 1.67. Depending on the state of the surface layer of crystals, the presence of internal defects in the crystal lattice, or isomorphic substitutions in the anionic and cationic sublattices, the Ca/P ratio can vary from 1.37 to 1.77 [6]. In our case, the deviation from the theoretically calculated value may be caused by the presence of magnesium cations in the sample.

| Element | O    | Mg  | P    | Ca   |
|---------|------|-----|------|------|
| Content, % | 39.46 | 5.19 | 21.24 | 34.10 |

The results of thermal analysis are shown in Figure 1. On the differential thermal analysis curve in the range from 25 to 1000 °C, 3 stages of thermal decomposition of the studied tusk sample can be distinguished. The formation of the first endothermic peak at 103 ºC is usually associated with the evaporation of external adsorbed moisture, and the completion of this process occurs at a temperature of about 200 ºC [10].
A more complex process of thermal destruction occurs in the temperature range from 200 to 600 °C. In this area, there is an endothermic process with a maximum at 350 °C, which, with a further increase in temperature, smoothly turns into an exothermic process. Authors of the work [10], when studying the processes of thermal destruction of bone and dental remains of animal and human tissues, showed, that in this temperature range oxidation and burning of the organic component occurs, the process is accompanied by the release of heat. The appearance of an endothermic effect at 350 °C may be due to the fact that the thermal analysis was performed in an inert environment. However, authors of the article [11] are not detected this effect during the thermal degradation process in an oxidizing environment. The study of thermal degradation of synthetic calcium-deficient, carbonate-substituted HAP is described by authors of the work [12]. The study revealed the appearance of two exothermic effects in the temperature range from 200 to 650 °C. The first process is associated with the evaporation of chemically bound water, and the second-with the release of carbon dioxide, which is formed as a result of partial cleavage of the carbonate anion from the structure of HAP. Thus, it should be assumed that the second endothermic peak observed in our work is probably related to the above-mentioned processes of evaporation of chemically bound water and the release of CO₂. However, for a more accurate explanation of the formation of the second endothermic peak, a thermal test with an analysis of the escaping gases should be performed.

At the third stage of thermal decomposition, we observe the formation of 3 small exothermic peaks at 686.9 °C, 794.3 °C, and 944.8 °C (Figure 1). These effects are probably related to the transformation of the structure of the mineral part of bioapatite of bone and dental tissues. However, results of the work [10] indicates that structural transformations in HAPs occur at a higher temperature - from 1000 °C and higher. Therefore, additional research is needed to determine the causes of these effects on the differential thermal analysis curve.

Thus, based on thermal analysis, it is established that the mass loss of the tusk sample is gradual, with a total mass loss of 38.32 %. Based on the data obtained, the quantitative composition of the studied tusk sample can be estimated as follows: external adsorbed moisture - 4.98 %, organic part - 27.51 %, mineral part - 67.51 %.

To identify the composition and structure of the mineral part of the tusk, XRD of samples was performed before and after heat treatment. The results of the XRD are shown in Figure 2.

On diffractograms of a mammoth tusk before heat treatment (Figure 2a), in the region of 30-35° angles 2θ, one main, widened peak is realized, indicating the predominance of an amorphous (low-crystalline) phase in intensity [13]. Identification by values of interplane distances and intensity of x-ray spectrum lines (2.793-100 %), (2.679-38.3 %), (3.425-33.9 %) corresponds to the mineral HAP $Ca_{10}(PO_4)_{6}(OH)_2$. The absence of other impurities confirms the fact that HAP in the process of long-term occurrence in permafrost retains its structure.
In turn, the analysis of the mammoth tusk diffractogram after heat treatment (Figure 2b) revealed that in the area of 30-35° angles 2θ one main peak becomes more intense, and the number of additional reflections increases, which indicates an increase in the crystallinity of the sample. The observed diffractogram, according to the interpretation in the PDF-2/Release 2011 database and the results described in the work [14], corresponds to the mineral whitlockite \(Ca_{x-x}Mg_x(PO_4)_2\). Proceeding from this it follows that in the process of heat treatment changes the structure of HAP from apatite in whitlockite.

The processes of dehydration and decomposition of HAP during heat treatment up to 1500°C depends significantly on the Ca/P ratio [15]. Authors of the article [16] showed that the presence and subsequent increase in the magnesium content in the structure of HAP leads to a decrease in the transition temperature of the apatite structure to the whitlockite structure. The destabilizing effect of magnesium is due to a noticeably smaller ion radius Mg$^{2+}$ (0.65 Å) compared with Ca$^{2+}$ (0.99 Å): substitution of a smaller ion leads to deformation of the crystal lattice, which contributes to the transition of hydroxyapatite-whitlockite. Thus, it can be assumed that the appearance of exothermic peaks at 686.9 °C, 794.3 °C, 944.8 °C on the differential thermal analysis curve (Figure 1) is due to the transformation of the structure of HAP due to the processes of dehydration and decarboxylation.

4. Conclusion
This study has shown that thermal destruction of mammoth tusk *Mammuthus Primigenius* is a multi-stage process in which three regions are distinguished: up to 200 °C evaporation of adsorbed water occurs; in the temperature range of 200-600 °C the organic part is burned out, which is accompanied by both endothermic and exothermic processes that lead to the most intensive reduction of the sample mass; in the region from 600 to 1000 °C, the appearance of 3 small exothermic peaks was noted, the appearance of which is due to the processes associated with the transformation of the structure of the mineral part of the mammoth tusk – HAP.

Using the XRD method, it was found that during the heat treatment of a mammoth tusk, the structure of its mineral part changes from apatite to whitlockite. It is also noted that due to the presence of magnesium ions in the crystal lattice of HAP, the transformation of its structure during heat treatment occurs at a lower temperature.

5. References
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**Acknowledgements**

The authors of this article express their gratitude to the staff of the Diamond and Precious Metal Geology Institute SB RAS Emelyanova N.N., Zayakina N.V., Vasileva T.I., Khristoforova N.V. for their help and assistance in conducting scientific tests. The work was performed as a part of the implementation of the State Assignment AAAA-A20-120011490003-9.