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Characterization of Elephant and Mammoth Ivory by Solid State NMR

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Ivory has always been considered one of the most attractive and valuable biological gem materials. It is the yellowish white, calcified, extremely elastic tissue that forms the tusks of several mammalian species. Microscopic examination of the surface in all possible directions is needed to a successful identification of cut and polished specimens of ivory, but sometimes it is not enough. Supplemental analytical techniques should be used for assisting discrimination of elephant (both Loxodonta africana and Elephas maximus) ivory and wholly mammoth (Mammuthus primigenius) ivory, because from a textural standpoint they can be remarkably similar. To provide the identifying key features of these two types of ivory is nowadays of special significance, due to the fact that elephant ivory trade and import and export are illegal, whereas wholly mammoth tusks may legally exported and manufactured. A discrimination between elephantine and mammoth ivory could therefore be of great importance as well. With this purpose, high resolution solid state NMR spectroscopy has been applied for the first time for the characterization of elephant and mammoth ivory. By exploiting ^{1}H, ^{13}C and ^{31}P magic angle spinning (MAS) NMR we investigated the composition of several specimens. The aim of the work is to find an experimental evidence which could highlight a significant diagnostic feature to discriminate between the two kinds of ivory. The multinuclear approach allows a detailed description of the nanostructured biomaterials from the point of view of the organic and inorganic phases. In particular, it provides a rich source of information about distances between the nuclei within the same nanophases and heterogeneous phases of hybrid structures. ^{13}C MAS NMR spectra collected with the single pulse experiment and the cross polarization technique at 300 MHz with 15 kHz spinning speed confirmed the presence of the CO_3^{2-} groups associated to the hydroxyapatite in both ivory types. In the collagen structure no differences have been highlighted. Quantitative ^{31}P MAS NMR spectra revealed important features about the inorganic matrix. Elephant ivory showed a single peak at about 3.1 ppm assigned to the bulk PO_4^{3-} groups of the hydroxyapatite phase. For the mammoth ivory the high resolution allowed us to achieve the simultaneous detection of the hydroxyapatite signal and of a smaller side peak at about 6.3 ppm ascribed to protonated PO_xH surface species. This minor signal could also be due to the presence of molecular water coordinated to the orthophosphate groups on the surface of the nano-sized hydroxyapatite crystals. The partial fossilization process in a frozen environment for more than 10000 years could explain the different NMR behaviour for the mammoth ivory. Solid state NMR spectroscopy could therefore be a useful tool for distinguishing between actual elephant ivory and mammoth ivory.