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Color origin and heat evidence of paleontological bones: Case study of blue and gray bones from San Josecito Cave, Mexico

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Abstract

Results of the investigation of paleontological blue and gray bone fragments of small vertebrates coming from stratigraphic layer 770 at San Josecito Cave (Nuevo Leon, Mexico, dating between 28 000 and 19 000 years BP), are presented. Structural and elemental analyses combining X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), and particle-induced X-ray and γ-ray emission (micro-PIXE/PIGE), as well as spectroscopic investigations [i.e., UV/visible/near-IR reflectance spectroscopy and X-ray absorption near-edge structure (XANES) spectroscopy] were performed to identify precisely the origin of the blue stain.

Prior research has shown that Mn^{5+} in tetrahedral coordination could be responsible for the turquoise blue color in mastodon ivory some tens of million years old that was modified by a heat process. Manganese is present in the anionic form of $(MnO_4)^{3-}$ and partially substitute for $(PO_4)^{3-}$ in the hydroxyapatite matrix.

The spectroscopic data of the present study have revealed a heat-induced modification, revealed traces of Mn among the typical bone constituents (Ca, P, Sr, Zn), and provided insights into the color origin of the blue paleontological bones from San Josecito Cave. Cations of Mn^{5+} in a tetrahedral environment of four O^{2-} ions in the apatite structure are found in these bones, the same color origin as in the blue mastodon ivory. As indicated by XANES, Mn^{4+} ions in octahedral coordination as in pyrolusite are found in gray bones. The presence of submicroscopic Mn oxide inclusions might explain the color of the San Josecito gray bones. The formation of Mn^{5+} very likely is induced by heat treatment of the bones under oxidizing conditions. The heat-induced modification of both types of paleontological bones also is indicated by the direct observation of apatite crystals using TEM. The question remains, however, how the heat originated inside the cave.

Keywords: Paleontological blue bone, TEM, XANES, color origin, Mn^{5+} apatite, heat-induced recrystallization